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ANILINE
AND ITS DERIVATIVES.

L O N D O N :

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ON
ANILINE

AND ITS DERIVATIVES.

A TREATISE UPON THE
MANUFACTURE OF ANILINE AND ANILINE COLOURS,

BY
M. REIMANN, P.D., L.A.M.

TO WHICH IS ADDED, IN AN APPENDIX,

"The Report on the Colouring Matters derived from Coal Tar, Shown at the French Exhibition, 1867." *By Dr. A. W. Hofmann, F.R.S., MM. G. de Laire, and Ch. Girard.*

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P R E F A C E .

DURING the last ten years the manufacture of Aniline and its coloured derivatives has grown from nothing to proportions never dreamed of by their discoverers. The hitherto unattainable brilliancy of these colours dazzled the public, and their popularity increased with astonishing rapidity. Simultaneously with the progress of Aniline industry, curiosity was naturally awakened as to the manufacturing details by which such bright colours could be obtained from coal.

The several steps of the Aniline manufacture have frequently been set forth, and the theories by which chemists account for the production of Aniline and the colours derived from it have been explained on several occasions. But none of these accounts, though many of them are trustworthy, give a clear representation of the actual state of the manufacture as adopted on a commercial scale. Nowhere do we find a plain statement of the methods of obtaining aniline and its derivatives, nor a description of the apparatus actually in use in manufactories.

The Author of the following treatise has made it his object to supply this want. He has endeavoured to give a comprehensive and accurate account of this industry as it is carried

on at the present time ; he has, moreover, given the previous methods of manufacture in an historical introduction, and the literature of the subject down to the most recent improvements has been fully laid under contribution.

The book has succeeded so well in Germany that the Author has been induced to prepare it for the English public. Whilst translating it he has not failed to incorporate in this English edition all improvements and observations made since the appearance of the German edition. Several new colouring matters recently introduced into commerce are described. Theoretical considerations have been strictly limited to those necessary to the clear understanding of the manufacturing processes spoken of.

As the sheets of Dr. Reimann's work were passing through the press, the very complete and valuable Report by Dr. Hofmann, F.R.S., MM. G. de Laire and Ch. Girard, "On the Colouring Matters derived from Coal Tar, shown at the French Exhibition, 1867," appeared in the *Moniteur Scientifique* of Dr. Quesneville. The contents of this were seen to be of such importance to all interested in the Aniline colour industry, that the Editor considered it advisable to translate, and give the whole Report in the form of an Appendix to the original book. A more appropriate addition to Dr. Reimann's work could not well be imagined, for whilst the Exhibition Report includes several novel facts and recent improvements which are as yet known to few but the reporters themselves, Dr. Reimann's work gives that explicit insight into the theoretical considerations and manufacturing operations which are required for a proper comprehension of this important branch of technical chemistry.

INTRODUCTION.

THEORETICAL Chemistry, properly so called, differs from Practical Chemistry in that it treats of all existing substances without exception, while Practical Chemistry treats only of those substances the production of which is capable of yielding a material advantage. It is clear, then, that Practical Chemistry constitutes only a part of Theoretical Chemistry.

Since Practical Chemistry becomes capable of making new observations only by means of its acquaintance with facts, it ought to make public its observations; for in this way only is it possible that among the vast number of scientific workers who thus gain additional knowledge, some particular individual, favoured by greater gifts or opportunities, may climb to a yet higher step of the great ladder. Were this always done there would be but one chemical science, enriched by the experiences both of the modest laboratory and of the great manufactory.

It is a false view to suppose that Theoretical Chemistry occupies itself only with observations made on a small scale. It is only because it is more convenient to make observations in this way that theoretical chemists employ small quantities, for it is in most cases indifferent whether

the reactions are effected in a platinum crucible or in a reverberatory furnace. In some cases, however, it is not unimportant; hence it would be foolish always to expect the same result from the crucible as from the furnace, and a well trained judgment will observe the difference in these particular cases.

Practical Chemistry, as exemplified in chemical manufacture, must always be in advance of the science, because in practice so much attention and energy is brought to bear on one point to produce a given result; it is the function of abstract scientific Chemistry to investigate the progress made, and to correlate the new observations with those previously known. Practical Chemistry can only advance by paying full regard to theory, and Scientific Chemistry can only progress by devoting proper attention to practice.

In the following Treatise I have endeavoured always to maintain a proper relation between practice and theory. Regarding the former as the pioneer of the science, I have treated in the first place of the purely empirical methods of manufacture discovered by actual experience, and have then proceeded to develop theoretical remarks.

Where theory has prepared the way for practice, I naturally give theory the preference, but in all cases theoretical speculations have been limited to those most important and really useful in practice. As regards the arrangement of the Treatise I simply follow the process of manufacture.

The distillation of tar has been passed over very briefly, because in most cases it is not effected by aniline manufacturers. The proper territory of aniline production is only entered with the manufacture of nitrobenzol.

M. REIMANN.

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ANILINE

AND ITS DERIVATIVES.

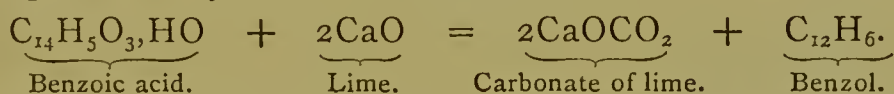
CHAPTER I.

BENZOL.

It is advisable to commence with this substance, as it may be considered the basis of the aniline industry.

Benzol, or benzine, may be obtained quite pure by distilling benzoic acid with three times its weight of hydrate of lime.

By the action of heat upon the acid, benzol is formed, whilst carbonic acid combines with the lime. The process is represented by the following equation:—



By this process the benzol is obtained as a colourless, very mobile fluid, of the specific gravity 0.85.

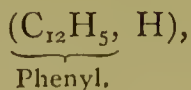
It boils at 85° C., and its vapour density is 2.38. Cooled to 0° it becomes solid, forming crystals which liquefy only at 7°. It is insoluble in water, but can be mixed with alcohol, or ether, in any proportion.

In its chemical character benzol may be considered as a compound of the organic radical phenyl (C_{12}H_5), with hydrogen, so that its constitution may be expressed by the formula $(\text{C}_{12}\text{H}_5)\text{H}$. Hence we may call it *phenylated hydrogen*.

In large quantities this substance is found in the products of the distillation of coal, and coal tar is the source whence we extract benzol for technical purposes. In the distillation of coal, three sorts of products are generally found:—At first gas is formed, and generally coals are distilled for the purpose of manufacturing illuminating gas. This gas consists of light and heavy hydrocarbons, especially the hydrocarbons C_4H_4 and C_2H_4 , carbonic acid, oxide of carbon, hydrogen, together with accidental admixture of nitrogen, &c. In the distillation of coal for gas a liquid is obtained in the receivers, which when investigated is found to consist of two different products, viz., coal tar and ammoniacal water. The latter can be easily separated from the tar, and is then used for making salts of ammonia: this need not be considered further here. The tar contains the substance now under discussion, viz., the benzol.

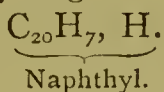
As is generally known, tar is a black, half liquid, half resinous mass of a bituminous odour. It is a mixture of a very great number of organic compounds, formed either directly or indirectly from the destructive distillation of coal. By repeated distillations the volatile contents of the tar can be easily separated from those which do not volatilise by heat.

On heating tar in a retort, benzol and other analogous substances, such as toluol, cumol, cymol, &c., are at first obtained. These compounds only differ from benzol in containing instead of the radical phenyl ($C_{12}H_5$) other radicals, such as tolyl, cumyl, cymyl, &c. After the benzol and its homologues have passed over, on continuing the heat a substance distils very similar to the common creosote obtained from wood. But the creosote obtained from coal tar has the property of crystallising; it is therefore sometimes called crystallised creosote. Its chemical names are phenic acid, carboic acid, or hydrate of oxide of phenyl. It contains the same radical as benzol, viz., phenyl; but while benzol is the compound of hydrogen with this radical,



phenic acid is the oxide of phenyl combined with one equivalent of water, or $C_{12}H_5O$, HO .

When the tar is freed from this substance also, by continuing the distillation another product is obtained which crystallises in large plates, and is apt to plug up the condensation tubes; hence much caution is necessary at this stage. This substance is naphthalin, a hydrocarbon which has the formula $C_{20}H_8$. This also is of analogous composition with benzol, for it is a combination of the organic radical naphthyl ($C_{20}H_7$) with hydrogen, and should properly be called naphthylated hydrogen.



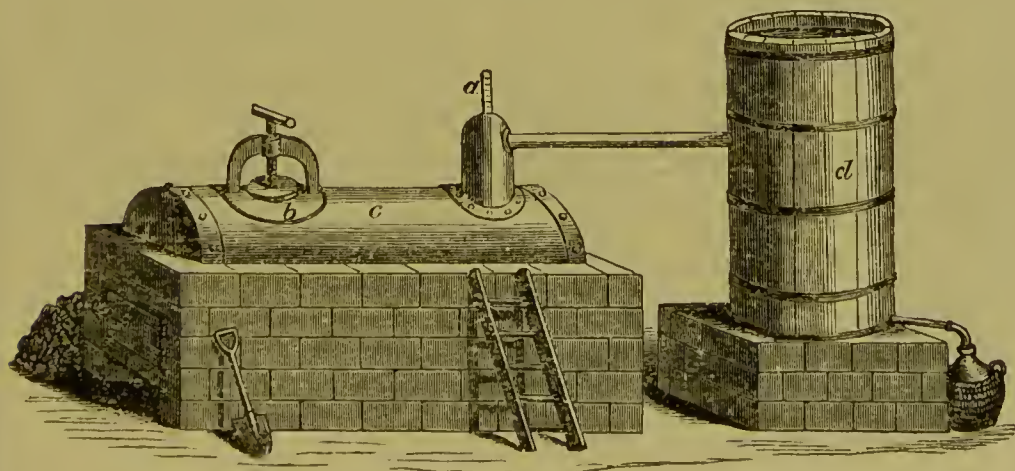
When no more naphthalin distils over, by again raising the temperature, a mixture is obtained of many hydrocarbons which have been only imperfectly investigated, and are sometimes sold under the name of photogen oil.

The retort now contains a black substance, solid when cold, and liquefied by heat; it is called asphalt.

The benzols obtained at first are called light hydrocarbons, to distinguish them from the heavy hydrocarbons, photogen and solar oil. The production of these two sorts of substances is usually effected separately.

The light hydrocarbons, *benzols*, are produced by manufacturers who wish to obtain asphalt for roofing, &c.

FIG. I.



a. Thermometer. *b* Opening closed by a screw. *c.* Boiler containing the tar. *d.* Cooling apparatus.

By distillation they separate the benzols from the other contents of the tar, and use the latter in their manufacture. The distillation is effected over an ordinary fire, in common boilers fitted with a cooling pipe. A thermometer is placed on the cupola of the boiler. At 80° C. the distillation commences. All products obtained from 80° to 100° are separately collected and preserved. When this temperature is exceeded the receiver is changed, and the products of distillation from 100° to 130° are received in the second vessel.

The benzols collected between 80° and 100° are called *light benzols*, those collected between 100° and 130° , *heavy benzols*. These two products are separately transformed into nitro-benzols, and we shall speak hereafter of light and heavy benzols, and of light and heavy anilines.

The benzols thus obtained consist principally of the hydrocarbons benzol and toluol, while cymol and cumol are present only in small quantities.

To give an idea of the contents of several species of coal tar I add here the results of investigations made on this subject by Dr. Crace Calvert.*

	Benzols.	Phenic acid.	Heavy hydrocarb.	Paraffin.	Naphthalin.	Dry tar.
The tar of Boghead coal contains.....	12	3	30	41	0	14 p.c.
„ Cannel „	9	14	40	0	15	22 „
„ Newcastle „	2	5	12	0	58	23 „
„ Staffordshire „	5	9	35	0	22	29 „

Latterly manufacturers have begun to distil benzol by means of steam. For this purpose steam is introduced into the tar through an iron tube, and the benzol is found in the receiver mixed with water. The benzol floats on the top, and may easily be separated pure. This method has the advantage of no fire being used, and all danger of ignition is thus done away with, but the separation of the light and heavy benzols is very difficult.

* Bulletin de la Soc. Ind. de Mulhouse, April, 1865. P. Schützenberger: L'histoire des Couleurs d'Aniline. Comptes Rendus, 16 August, 1859, p. 263.

Instead of worms, double cylinders are often used to cool the benzol vapour, cold water circulating in the intermediate space, while the benzol is condensed inside. But I think worm's are better, on account of their simplicity and cheapness. For the distillation of naphthalin, however, the above-mentioned cylinders are to be preferred, because they cannot be easily obstructed by the naphthalin crystals.

CHAPTER II.

NITRO-BENZOL.

WHEN benzol is mixed with nitric acid it is changed into a yellow liquid which has a strong smell of bitter almonds. The substance thus obtained is nitro-benzol. It was produced on a large scale before it was used in the manufacture of aniline as a substitute for bitter almond oil, and was employed in perfumeries under the name of Essence of Mirbane or *Huile de Mirbane*.

It has already been mentioned that there is a series of benzol compounds boiling at different temperatures ranging from 80° to 130° C. It is therefore natural that there should be a corresponding series of nitro-benzols, boiling from 205° to 235° , though the substance properly called nitro-benzol by chemists, boils constantly at 213° . It was shown before that the liquid obtained from coal tar, and commonly called benzol, consists of a series of hydrogen compounds of phenyl, tolyl, cumyl, cymyl, &c., and that after treating this mixture with nitric acid we get the respective nitro-compounds of the same hydrocarbons. It must be still remarked that there is a difference between the nitro-benzols distilling at 205° to 210° , those which distil at from 210° to 220° , and those which distil from 220° to 230° . If the benzols are separately treated with nitric acid, the benzol distilling at from 80° to 100° , and that obtained at from 100° to 130° , will differ considerably in their smell. The benzol first obtained will yield a nitro-benzol of a pure and agreeable

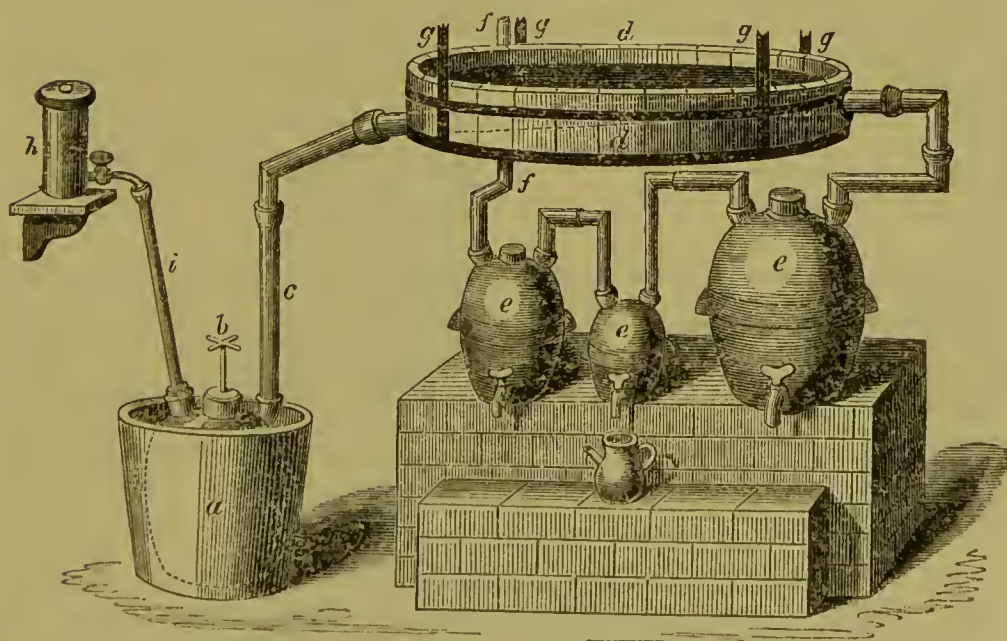
odour resembling that of bitter almonds, that distilled between 100° and 130° will yield a nitro-benzol which has a disagreeable odour. It is therefore only the first product that can be used for the purposes of perfumery. The first kind of nitro-benzol is comparatively pure, while the other kind contains nitro-toluol; nitro-cumol, and nitro-cymol being also present in smaller quantities.

To manufacture Essence of Mirbane for perfumery a glass worm-pipe is employed, divided at its upper part in the form of a fork; the whole being surrounded with cold water. Into one of the fork-like branches is poured a mixture of sulphuric and nitric acids, the other branch being fed with benzol. Both the liquids mix in the worm-pipe, and the heat given off is carried away by the surrounding water.

Having passed the pipe, the mixture of nitro-benzol, benzol, and the excess of the acids, falls into a vessel filled with cold water. The excess of acid is there separated from the nitro-benzol, which is thus obtained pure.

To produce nitro-benzol on the large scale necessary in the manufacture of aniline, the above-mentioned apparatus cannot be used.

FIG. 2.

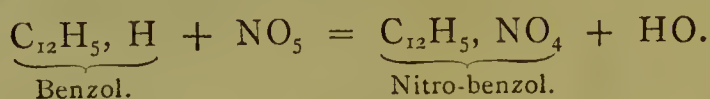


a. Woulff's bottle. *b.* Agitator. *c.* Leading pipe for the vapours. *d.* Vat. *e.* Woulff's bottles containing water. *f.* Exit pipe. *g.* Holders of the vat. *h.* Bottle with the mixtures of acids.

At first earthen vessels were employed for manufacturing the nitro-benzol. A Woulff's bottle thoroughly cooled with water, is filled with the benzol, to which a mixture of sulphuric and nitric acids is added in a small stream. As may be seen in the annexed drawing (Fig. 1), a bent glass tube is put into the bottle to agitate the liquid. From time to time a workman moves this agitator, and mixes the substances contained in the Woulff's bottle. One neck of the bottle is connected by a tube to the vessel that contains the mixture of nitric and sulphuric acids. Instead of mixing the two acids before introducing them into the bottle, they may be led from two separate bottles into a funnel, where they are mixed, and pass immediately into the pipe leading to the Woulff's bottle. Into the middle neck is fixed the agitator so that it can be moved, and the third neck bears a tube of earthenware, which leads (*see* drawing) through a vat filled with water, so that the condensed vapours may run back into the bottle. After passing the vat, the tube is bent down to a small Woulff's bottle filled with water, by which the uncondensed vapours (chiefly NO_3) are led through several Woulff's bottles before passing to the chimney.

The bottle is set in a wooden vat through which a current of cold water or of steam may be led.

By treating benzol with nitric acid, nitro-benzol and water are formed, thus :—



On the production of nitro-benzol, water is always formed ; this when free would dilute the nitric acid so much that it would be no longer strong enough to transform the benzol, since only strong nitric acid can effect this change. Hence we always add to the nitric acid a quantity of sulphuric acid, which combines with the water formed at the moment of change.

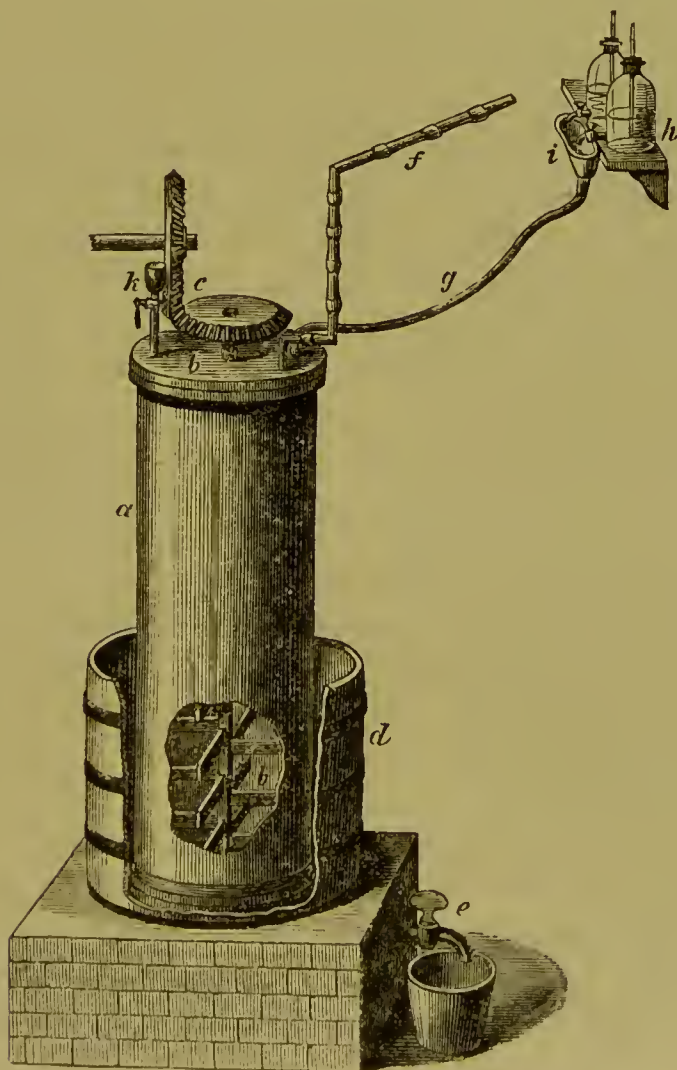
At the commencement of the process cold water is led through the vat surrounding the bottle ; but when the greater portion of the nitric acid has been added, and the first violent action is over, by passing steam into the vat this water is

gradually heated, and now the last reaction is effected on the benzol remaining in the bottle.

As the manufacture of aniline increased, the Woulff's bottle was found too small to produce nitro-benzol on a sufficiently large scale. These vessels of earthenware were also so fragile that it was dangerous to work with them. Hence aniline manufacturers had to choose other vessels.

Iron is attacked by most acids, also by nitric acid when diluted; but if the nitric acid is very concentrated and evolves yellow vapours, iron is no longer affected by it; neither does a mixture of nitric and sulphuric acids affect iron. Hence, for making nitro-benzol, manufacturers now use large iron cylinders, in which an iron agitator is fixed, as shown in Fig. 3. This agitator is moved by a pair of

FIG. 3.



wheels. The benzol is introduced through an opening in the lid of the cylinder, after which the opening is closed. Through another opening in the lid a glass tube passes, which serves to introduce the mixture of sulphuric and nitric acids into the cylinder. A third opening admits a tube of earthenware, which conducts the vapours, formed by the action of nitric acid on the benzol, to a long cooling pipe. At the bottom of the cylinder an iron pipe leads to an earthenware tap, through which the nitro-benzol can be drawn off. The cylinder is surrounded by an iron vessel containing water. This water is also renewed at the commencement, and heated towards the close of the operation. After filling the cylinder for a quarter of its height with benzol, and having begun to agitate, the mixture of acids is introduced through the above pipe. Gradually the contents of the cylinder become heated, which heat is prevented from becoming too strong by changing the water in the surrounding vessel. When the whole quantity of nitric acid has passed into the cylinder the surrounding water is heated, whereby the remaining benzol is transformed into nitro-benzol. When the action is over, the contents of the cylinder are drawn off through the tap, and washed with water. This washing dissolves out the acids from the nitro-benzol. The nitro-benzol sinks to the bottom of the vessel containing the water, and the contents of the cylinder can be collected by means of a separating funnel. It is then ready to be used for making aniline.

To obtain nitro-benzol on a large scale, 12 parts of benzol are employed, together with a mixture of 13 parts of fuming nitric acid and 8 parts of sulphuric acid.

The nitro-benzol obtained as before-mentioned is pure enough for the manufacture of aniline; but if it is to be used as a substitute for oil of bitter almonds, it must be once more distilled by means of steam. The nitro-benzol is, in this case, put into an iron retort heated from below, and superheated steam is passed through the nitro-benzol. A distillate is obtained which contains water and nitro-benzol; the latter soon sinks to the bottom.

The reason why the mixture of nitric acid and benzol must be cooled, is to prevent a too sudden and strong reaction

of the nitric acid on the benzol. When too strong this reaction no longer yields pure nitro-benzol, but another product, differing from nitro-benzol by containing one equivalent more of nitrous acid. This product is binitro-benzol $C_{12}H_4(NO_4)_2$.

This is not actually injurious, but by its transformation into aniline nitraniline is formed, which is quite useless in the manufacture of aniline colours. As may be easily shown, binitro-benzol has a greater density than common nitro-benzol, and also nitraniline is heavier than common aniline. But being useless in the manufacture of aniline colours, nitraniline can only be looked upon as so much loss and a diluent of true nitro-benzol.

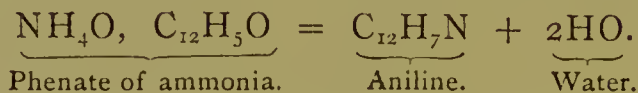
CHAPTER III.

ANILINE.

ANILINE is found already formed in coal tar. M. Runge enumerated among the alkaline products of coal tar, pyrrhol, aniline (called by him cyanol), and leukoline. Picoline, naphthalin, and paranaphthalin were also found by MM. Anderson and Anders. The aniline in tar is the product of the action of phenic acid on ammonia. At first these two substances yield a compound phenate of ammonia



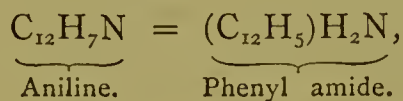
which at a high pressure is transformed into aniline and water,



By treating the heavy hydrocarbons with dilute hydrochloric acid aniline is dissolved from them in the form of hydrochlorate, which can be obtained in the dry state by evaporating the solution. From this salt aniline may be easily got by distillation with lime or potash. In the tar oils a small quantity of this substance remains, but much too small to allow it to be extracted profitably. Hence aniline must be produced artificially. Analogous to the probable formation of aniline from the phenate of ammonia, this salt may be submitted to high pressure by heating in sealed

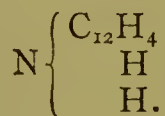
iron vessels, whereby it is changed into aniline and water. This method of producing aniline is a discovery of MM. Hofmann and Laurent. Till now, however, they have not succeeded in employing it for technical purposes.*

This mode of producing aniline led the discoverer to consider it an amide of the organic radical phenyl,

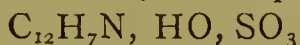


and to call it phenylamide.

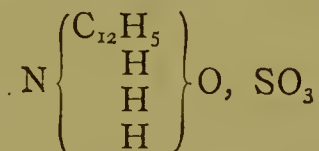
We may then consider aniline to be an ammonia in which one equivalent of hydrogen is replaced by the radical phenyl,



As the ammonia itself combines when forming salts with one equivalent of hydrogen to form the hypothetical metal ammonium NH_4 , so does aniline or phenylamine also unite with one equivalent of water when it combines with an acid to form a salt. For instance, the sulphate of aniline



is represented by the formula



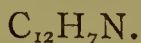
Long before M. Runge discovered aniline in coal tar, M. Unverdorben, the first discoverer of this base, produced it in 1826 by heating indigo. M. Fritzsche showed in 1840 that by treating indigo with a solution of caustic potash, by which process indigo is transformed into anthranilic acid, and, after drying, heating the mass thus obtained, aniline might be got. Isatate of potash also yields aniline by heat.

It is almost unnecessary to say that none of these methods of producing aniline can be used to manufacture it on the large scale; indeed the only method of producing aniline for commercial purposes is that of the reduction of nitrobenzol.

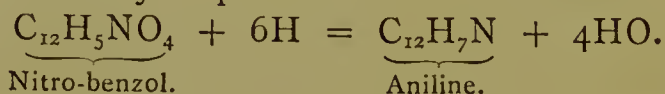
* A. W. HOFMANN, "Reports by the Juries." London, 1863.

As mentioned above, the formula of nitro-benzol is

$$\text{C}_{12}\text{H}_5\text{NO}_4,$$
 and that of aniline



The two substances differ from one another only by the addition of 2 equivalents of hydrogen and the subtraction of 4 equivalents of oxygen, the quantities of carbon and nitrogen being equal. It will, therefore, be easily understood that by adding 6 equivalents of hydrogen to nitro-benzol, aniline may be produced—



Already in 1842* M. Zinin found that by adding sulphide of ammonium to a solution of nitro-benzol in alcohol, an organic base could be produced which he called benzidam, and which M. Fritzsche proved later to be identical with aniline.

In 1854 M. Béchamp found that ferrous salts of weak acids, such as the acetate of the protoxide of iron, could be used for reducing nitro-benzol, by transforming it into aniline. He employed directly iron filings, and acetic acid in which the nitro-benzol was dissolved.

The best proportions† were found to be 1 part of nitro-benzol to 1·2 parts of iron.

This method is now the only one used in the manufacture of aniline on the large scale.

The apparatus employed for this manufacture consists of a closed iron cylinder (Fig. 4), in which an iron agitator works. An iron tube, *g*, conducts from the lid of the cylinder to a worm, while another iron tube, *d*, entering the apparatus, reaches almost down to the bottom, and serves to introduce steam from a boiler. On the lid of the cylinder an iron funnel, *k*, is placed, which can be stopped with a wooden plug; this serves to introduce iron filings. Finally, through the lid a tube, *i*, enters the cylinder, for introducing a mixture of acetic acid and nitro-benzol.

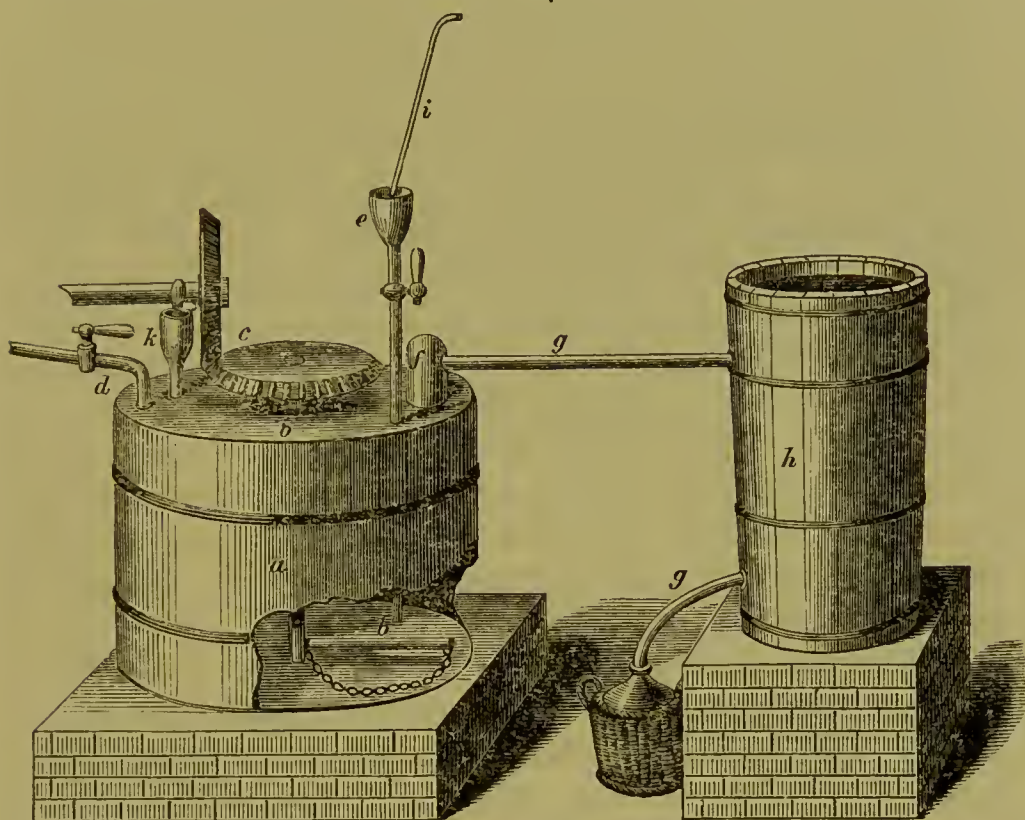
At first a portion of iron filings is introduced into the apparatus, together with a little water. On this a quantity of

* ERDMANN, Journ. f. pr. Chem., vol. 62, p. 469.

† HOFMANN found in 1856, that it was better to use 2·5 parts of iron. ERDMANN, Journ. f. pr. Chem., vol. 67, p. 131.

the strong acetic mixture is poured, and as the reaction becomes more vehement more acetic acid and nitro-benzol is added, together with, sometimes, a little water. When the

FIG. 4.



a. Iron cylinder. *b.* Lid of the iron cylinder. *c.* Wheels. *d.* Tube introducing steam. *e.* Iron funnel with tap. *f.* Cupola. *g.* Cooling pipe. *h.* Vat. *i.* Pipe for introducing the acid. *k.* Iron funnel with wooden stopper for introducing the iron filings.

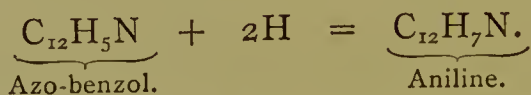
action becomes quieter more iron filings are introduced. The quantities used are as follows:—150 parts of wrought iron, 100 parts of nitro-benzol, and 50 parts of strong acetic acid made from wood. On commencing the manufacture it will be well to take 100 parts of acetic acid, as the working is easier with this larger quantity. Afterwards it may be diminished to 50. During the whole operation agitation must be continued.

The heat produced by the reaction of the different substances is not sufficient to change all the nitro-benzol into aniline, and the transformation must be completed by the introduction of steam at the end of the operation. This will cause a certain part of the contents of the cylinder to distil

over; it may be caught in a receiver, and re-introduced into the apparatus, until no more undecomposed nitro-benzol is found in the distillate. When this is found to consist only of aniline, water, and acetic acid, the operation may be considered complete, and the contents of the apparatus are now distilled until only oxide of iron remains behind.

In this operation acetic acid and iron are transformed, by the decomposition of water, into acetate of the protoxide of iron, which, under the influence of heat and the oxygen in the nitro-benzol, is transformed into acetate of the peroxide of iron, and then to hydrated oxide of iron. The aniline, which is a base, as we have shown, similar to ammonia, combines with acetic acid, but by distillation the compound is destroyed, and in the receiver a very dilute solution of acetic acid and aniline oil is collected, which latter after some time separates from the water and may be taken off. In a well conducted operation 66 parts of aniline may be obtained from 100 parts of nitro-benzol. Theory demands 75, but this result is never attained in practice.

In case too much iron filings have been used, there is not so much as 66 per cent of aniline obtained, and after finishing the operation and opening the cylinder there will be found a tarry brown mass mixed with the oxide of iron. This substance is produced by the too rapid reduction of nitro-benzol, and the removal of oxygen from the combination without touching the hydrogen. M. Mitscherlich, who discovered this substance in 1834,* called it azobenzol—because it consists of a combination of nitrogen (azote) and the radical phenyl—($C_{12}H_5$, N). It is possible to transform the azobenzol into aniline by adding two equivalents of hydrogen;



This is effected by treating it with ammonia and sulphuretted hydrogen gas.

By saturating the distillate, after separating the aniline from it, with soda, and evaporating, acetate of soda is produced.

* POGGEND. Ann., vol. xxxii., p. 224.

Previous to the employment of the above method of producing aniline, nitro-benzol was reduced by a mixture of hydrochloric acid and iron; in this case the process is the same, except that hydrochloric acid is substituted for acetic acid.

As hydrochloric acid is much cheaper than acetic acid, the process ought to be more economical. But nitro-benzol will not mix with hydrochloric acid, though it will easily with acetic acid; hence, at the same time, alcohol must be added to the mixture, in order to dissolve the nitro-benzol, and enable it to be transformed into aniline. In this case the aniline is obtained in the form of a hydrochlorate, which being a very stable salt, must be decomposed by distillation with lime. After the operation in the above-mentioned apparatus is finished, the whole contents must therefore be transferred to another retort, where the alcohol is distilled off, hydrochlorate of aniline and chloride of iron remaining. The dry mass of these two substances must then be mixed with lime, and again distilled with steam to obtain the pure aniline.

The single operation described above is in this manner extended to three, and a considerable loss of time and of alcohol always takes place. The method is therefore now abandoned in all aniline manufactories, the only one employed being that with iron and acetic acid.

After this description of the methods of producing aniline oil on a large scale, we will now give other methods proposed by different chemists to manufacture aniline, which though now not used on a large scale, may still become useful in the future.

In 1863, M. Kremer* found that aniline might be obtained by heating nitro-benzol with water and zinc powder as obtained in zinc manufactories,† oxide of zinc being formed. From 100 parts of nitro-benzol he obtained 63 to 65 parts of aniline. Zinc powder being at the present time cheap, this method may possibly be economically employed.

Finally, M. C. Wöhler‡ proposed, as early as 1857, to

* DINGLER'S Polyt. Journ., 169, p. 377. ERDMANN, Journ. f. pr. Chem., vol. 90, p. 254.

† DINGLER'S Polyt. Journ., vol. 168, p. 158; Polyt. Centralbl., 1862, p. 830.

‡ ERDMANN Journ., f. pr. Chem., vol. 71, p. 254.

transform nitro-benzol into aniline by means of an alkaline solution of arsenious acid. M. Wöhler introduced a thin current of nitro-benzol into a retort in which was boiling a solution of arsenious acid in very strong potash (36° of Beaumé). Aniline distilled over mixed with water, whilst there remained in the retort a solution of arseniate of potash.

Theoretically considered, aniline belongs to the large number of organic compounds which are called amide bases, because they all have a composition similar to ammonia, one equivalent of the hydrogen being replaced in them by an organic radical.

We know many series of organic radicals whose formulæ correspond, and to one of these series belong the radicals of the substances which form aniline oil.

The algebraic type for these radicals is $C_{2n}H_{2n-7}$. The series of radicals belonging to this type is—

$C_{12}H_5$ Phenyl.

$C_{14}H_7$ Tolyl.

$C_{16}H_9$ Xylyl.

$C_{18}H_{11}$ Cumyl.

$C_{20}H_{13}$ Cymyl.

By the combination of one equivalent of hydrogen with these radicals various substances are formed, some of which have been already mentioned ;

$C_{12}H_5, H =$ Benzol.

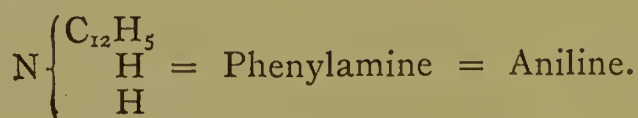
$C_{14}H_7, H =$ Toluol.

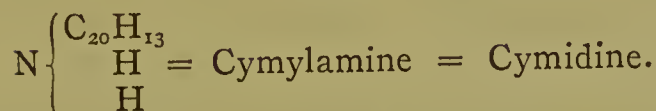
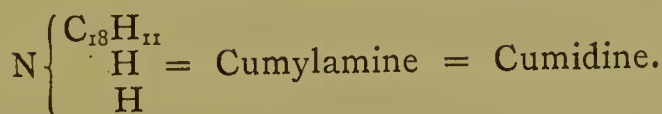
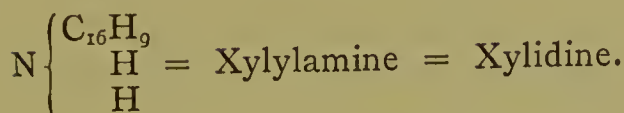
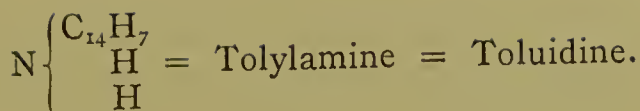
$C_{16}H_9, H =$ Xylol.

$C_{18}H_{11}, H =$ Cumol.

$C_{20}H_{13}, H =$ Cymol.

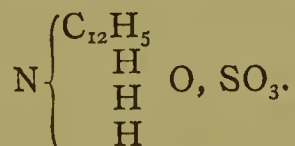
When these radicals occur in combination similar to that of ammonia (NH_3), so that one equivalent of the hydrogen of this substance may be viewed as being replaced by one of radical, the bases are formed of which commercial aniline oil consists,—





All these substances are bases, and are very similar to one another.

When combined with acids, aniline and its homologues unite with one equivalent of water, so that we must write sulphate of aniline, for instance,



Before speaking of aniline oil in general, it will be well to describe particularly the various substances of which it consists. The first of which we will speak is aniline.

Aniline when pure is a colourless mobile oil, which can be cooled to -20°C. without freezing. Its specific gravity at 16°C. is 1.020. It boils at 182°C. It volatilises at the ordinary temperature of the atmosphere, and if dropped on paper disappears after some time. It can be mixed with alcohol, ether, aldehyd, and volatile and fixed oils in every proportion. It is slightly soluble in water, from which it may be precipitated by common salt. When lighted it burns with a large smoky flame, and must therefore be regarded as a dangerous combustibile. When exposed to the atmosphere it assumes a red colour, which disappears again on distillation. It is somewhat poisonous.

Of the reactions of aniline, the most delicate is that produced with hypochlorites. Aniline added to a solution of bleaching powder in water produces a blue-violet colour,

changed by acids to red. One of the discoverers of aniline, M. Runge, was well acquainted with this reaction.

Dilute sulphuric acid yields with aniline or with a solution of an aniline salt, a white or reddish precipitate of sulphate of aniline. If aniline is employed, the whole solution changes into a white magma.

Hydrochloric acid yields with pure aniline a magma of crystals.

A glass rod moistened with hydrochloric acid produces when held over aniline a white cloud of hydrochlorate of aniline.

Nitric acid mixed with aniline yields after some time blue and green efflorescences.

Aniline is expelled from its salts by alkalis, and also by ammonia at the ordinary temperature, but when heated aniline expels ammonia from its salts.

When aniline or a salt of this base is mixed with some drops of sulphuric acid, and a little bichromate of potash is added, an evanescent blue colour is produced.

Albumen is coagulated by aniline. Pine wood and alder pith when moistened with solutions of aniline salts assume a dark yellow colour, which is not attacked by chlorine. According to M. Runge, this colour is apparent when only 1-500,000th of aniline is present.

To obtain perfectly pure aniline, common aniline is distilled several times to remove the tarry substances, and the colourless oil thus obtained is mixed with a solution of oxalic acid in alcohol. After some hours oxalate of aniline crystallises from the liquid, and this when dissolved and re-crystallised several times, yields by distillation with potash pure aniline.

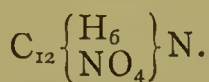
Sulphate of aniline, $C_{12}H_7N$, HO , SO_3 , when dry, is a white crystalline powder, which takes a reddish hue when exposed to the atmosphere. Upon heating it, water mixed with aniline volatilises, an acid sulphate of aniline remaining. On continuing the heat, it yields a mixture of sulphite of aniline, ammonia, and odourine.

Sulphate of aniline is difficultly soluble in cold water, easily in hot. It is almost absolutely insoluble in ether, and is

with difficulty soluble in pure alcohol, but more easily in dilute spirit.

When mixed with nitric acid, aniline yields nitrate of aniline, $C_{12}H_7N$, $HO NO_5$, as a crystalline mass.

Nitraniline is a substance produced by the substitution of one equivalent of hydrogen in aniline by nitric peroxide (NO_4), and is therefore expressed by the formula

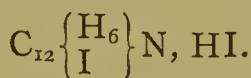


It occurs in long needles of a beautiful yellow colour, which being heavier than water sink to the bottom. They liquefy at $110^\circ C.$ to a yellow oil, which boils at $285^\circ C.$ Nitraniline has a burning sweet taste. Its reaction is neutral, although it can combine with acids to form real salts. It dyes pine wood yellow, but is not itself coloured by bleaching powder.

It is produced by treating dinitro-benzol with reducing agents, as above described. (See page 11.) It was discovered in 1846 by Hofmann and Muspratt.

Hydrochlorate of aniline may be easily produced by adding hydrochloric acid to aniline. Its formula is $C_{12}H_7N$, HCl . It is easily soluble in alcohol or water. Its reaction is acid.

A solution of iodine in aniline soon forms crystals of hydriodate of aniline, $C_{12}H_7N, HI$, and the solution contains also the hydriodate of ioduretted aniline,



No compound of aniline with carbonic acid is known.

The combination of aniline with acetic acid cannot be crystallised; it volatilises with the vapour of water, in which operation it is decomposed.

Toluidine is contained in all the aniline oils of commerce. It was discovered in 1845 by MM. Hofmann and Muspratt,* and is obtained by reducing nitro-toluol. Common nitro-benzol being a mixture of nitro-benzol and nitro-toluol, aniline and toluidine together are obtained from it by reduction.

* Annal. d. Chem. u. Pharm., vol. liv., p. 1.

According to the investigations of M. Chautard,* it can be got by distilling the resin produced on treating oil of turpentine with nitric acid, with a solution of potash.

I have found that toluidine can be got directly from crude aniline oil by transforming it by means of oxalic acid into oxalates, and treating the mixture of these salts with ether. This dissolves all other oxalates except oxalate of toluidine.

By crystallising this salt it may be purified, and when distilled with potash it yields pure toluidine. Toluidine occurs in large colourless crystalline plates, which liquefy at 40° C. and boil at 198° . Like aniline, it volatilises at the common temperature of the air. It has a burning taste.

With hydrochloric acid vapour toluidine yields clouds of hydrochlorate of toluidine similar to those of aniline. By a solution of bleaching powder it is dyed red, differing in this respect from aniline.

Toluidine, also, in acid solution, dyes pine wood and alder pith yellow, just as aniline does. By decomposing the salts of toluidine with an alkali, this base is obtained in the form of a coagulum which rises to the top of the liquid. It is soluble in wood spirit, alcohol, ether, aceton, and also in volatile and fat oils. The formula of toluidine is, as before mentioned, $C_{14}H_9N$.

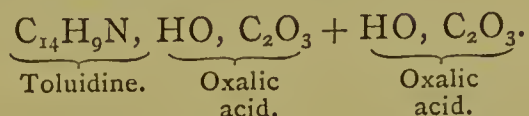
Sulphate of toluidine can be obtained by adding some drops of sulphuric acid to a solution of the base in ether. The white crystalline precipitate thus obtained is washed with ether and crystallised from water. It is easily soluble in water. This constitutes a difference between it and the sulphate of aniline.

The hydrochlorate of toluidine is obtained as the corresponding aniline salt; it can be got in white crystalline plates, which soon acquire a yellow tinge in the atmosphere. It is easily soluble in water and alcohol, but with difficulty in ether. Its solution has an acid reaction.

A solution of toluidine in alcohol, when mixed with a

* N. J. Pharm., 24, 166. Journ. f. Pract. Chem., 60, 240.

similar solution of oxalic acid, yields brilliant white needles of binoxalate of toluidine,



This salt is difficultly soluble in cold water and alcohol; more easily when the liquids are boiling.

Chinoline exists in general only in aniline oils got direct from heavy oil of tar. It was discovered in coal tar by M. Runge* in 1834. He called it leukol, while M. Gerhardt,† who obtained the same body by distillation of quinine and quinidine with hydrated potash, called it chinoline. To get pure chinoline, heavy tar oils are treated with hydrochloric acid; the solutions of hydrochlorates are then evaporated, and the dry salts distilled with milk of lime. The distillate which first passes over is collected separately until it no longer turns bleaching powder blue. As soon as the colour of the bleaching powder ceases to be affected by the distillate, the receiver is changed and the oil now distilling is collected; this consists almost entirely of chinoline. After dissolving it in alcohol an alcoholic solution of oxalic acid is added, which causes, after some hours, a precipitate of oxalate of aniline, the oxalate of chinoline remaining in solution. After separating the crystals from the liquid the latter is distilled with lime, whereby first alcohol and then chinoline is obtained; the latter is freed from water by a second distillation over chloride of calcium. The pure chinoline thus obtained is a colourless oil of the specific gravity of 1.081 at 10° C. It boils at 239°. Its odour is penetrating, and similar to that of bitter almonds; it is slightly poisonous.

Chinoline is not coloured by bleaching powder, neither does it dye pine wood. It yields, when treated with a mixture of chlorate of potash and hydrochloric acid, an orange coloured oil which becomes resinous when cold. This substance is dissolved by hot alcohol, and precipitated again when the alcohol cools. Aniline expels chinoline from its salts.

* Poggend. Ann., 31, 68.

† Journ. f. pr. Chem., 28, 76.

Chinoline is soluble in every proportion in bisulphide of carbon, alcohol, ether, acetone, aldehyde, but is with difficulty soluble in water. It is dissolved both by volatile and fixed oils.

The formula of this substance is $C_{18}H_7N$, and the radical contained in it has therefore the composition $C_{18}H_5$.

Sulphate of chinoline, consisting of sulphuric acid, the base, and one equivalent of water, can be easily got by dissolving chinoline in ether and adding sulphuric acid. A thick liquid immediately sinks down, which after some days solidifies to a mass of microscopic crystals.

By treating chinoline with hydrochloric and oxalic acids, difficultly crystallising salts are obtained which correspond in composition with the similar salts of toluidine.

Odorine is a base of the same composition as aniline. It was discovered in 1826 by M. Unverdorben,* who found it in the oil distilled from bones (*oleum animale fœtidum*). On account of its very disagreeable penetrating smell he called this oil odorine. In 1846, Mr. Anderson once more investigated this oil and called it picoline.

This substance is contained only in very small quantities in the tar oils, and in still smaller quantity in aniline oil, but there is quite sufficient present to give a very disagreeable odour to the common aniline oil. To obtain this substance pure is very difficult, and, according to Mr. Anderson, it is effected as follows:—The oil obtained on the rectification of tar oil is mixed with sulphuric acid, which saturates the bases, forming the corresponding sulphates. This solution of the bases in sulphuric acid is separated from the tar oil and mixed with common ammoniacal liquid obtained in the distillation of coal. Upon distilling this mixture water is at first obtained, and then a thick dark brown oil heavier than water, consisting substantially of odorine, aniline, pyrrol, and benzol, and also of a heavy thick oil of a neutral reaction. Three-fourths of this oil are distilled over, and the last fourth is left in the retort. It consists of the above-mentioned neutral oil.

* Poggend. Ann., 8, 259 and 480; 11, 59.

The distillate is a mixture of water, odorine, and a little aniline; it is supersaturated with sulphuric acid, and distilled. In this way a solution of pyrrhol in water is obtained, and the sulphate remaining in the retort is then supersaturated with hydrate of potash and heated, whereupon a solution of odorine in water distils over. To this, hydrate of potash is added, which effects the precipitation of the pure odorine.

Odorine boils at 133° C., and its specific gravity at 10° is 0.955. Its smell is excessively disagreeable. It does not dye alder pith, pine wood, or become coloured by bleaching powder. Hydrochloric acid when held over odorine gives rise to clouds of white hydrochlorate of odorine. It mixes in every proportion with alcohol, ether, fixed and volatile oils, and even with water, by which latter circumstance it differs from every other similarly composed substance.

The composition of odorine is similar to that of aniline, viz., $C_{12}H_7N$.

From an oil which MM. Collin and Coblentz had obtained by distilling aniline, and which boiled only at a very high temperature, Dr. Hofmann produced a new base. He treated a portion of this oil which distilled at a temperature above 333° with sulphuric acid, and washed the resulting sulphates with water, whereby he separated an easily soluble from a difficultly soluble sulphate. The latter yielded when decomposed by soda a thick basic oil which solidified after some days. After pressing it in bibulous paper this substance was crystallised, when it deposited in bright, silk-like needles which liquefied at a temperature of 192° , and boiled at 360° . Analysis gave the formula $C_{12}H_7N$.

This substance has therefore the same formula as aniline, but differs from it in properties; hence it may be called "paraniline."

Paraniline forms well defined crystals, and Dr. Hofmann thinks that paraniline may be obtained from aniline by submitting this latter to a very elevated temperature.

Common Aniline Oil is never pure aniline but always a mixture of aniline, toluidine, odorine, &c. It is commonly free from chinoline, which is contained only in the oil immediately obtained from coal tar.

Aniline oil is a yellow or brown fluid of a peculiar disagreeable smell, sometimes, especially when obtained directly from coal tar, of a common photogen smell. It takes fire easily, and must be very cautiously preserved. It is usually sold in iron bottles surrounded with basket-work. Each iron flask usually contains one cwt. of oil.

Aniline oil begins to boil at 175° or 180° C., and almost entirely distils between 180° and 205° . Common aniline oil never has a constant boiling point, but in every case a thermometer put into the boiling fluid rises degree after degree as ebullition progresses. By comparison of the boiling points of the substances contained in aniline oil (odorine 133° , aniline 182° , toluidine 198° , chinoline 239°), we find that aniline oils boiling at a low temperature must contain an excess of undecomposed benzol and odorine. The higher boiling points are those of mixtures containing a larger proportion of toluidine mixed perhaps with the more difficultly boiling homologues of aniline, viz., chinoline and some of the heavy tar oils. Undecomposed nitro-benzol also elevates the boiling point of aniline oil. When it begins to boil, aniline oil yields a little water and benzol. If these do not average more than from 2 to 4 per cent, no adulteration need be suspected.

It is of the greatest importance for every colour manufacturer to know as readily as possible the quality of an aniline oil which he proposes to use in making colours. But up to the year 1867 there was no method of investigating the colorific power of aniline oil, especially with reference to magenta.

In this year I made considerable investigations on this subject, and was so fortunate as to find a method which, in from a quarter to half an hour, will detect whether an aniline oil is capable of producing a large or small quantity of magenta, and which also points out how the defective oil may be ameliorated.

This method enables one to render available an aniline oil which otherwise could not be used for producing colours, by a simple mixture with another oil.

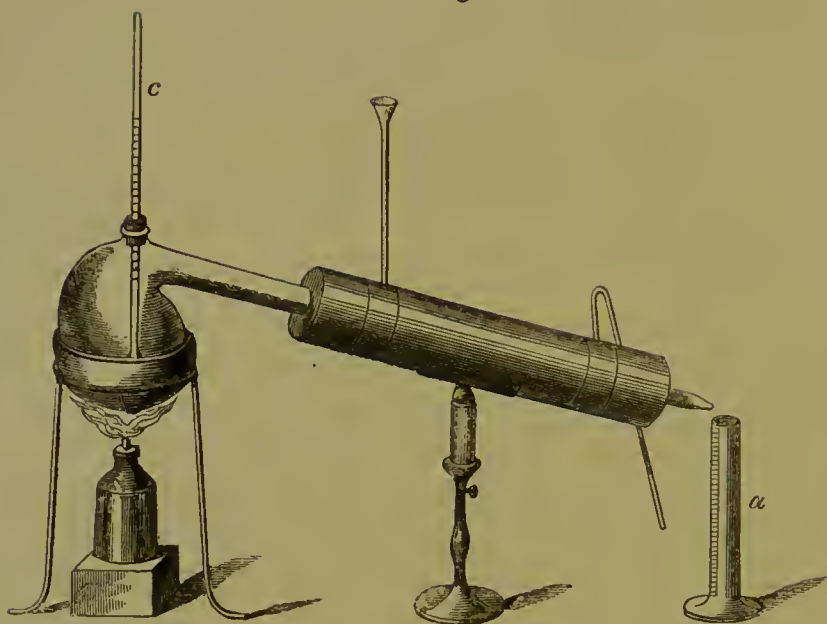
The method which I discovered is so simple that it is strange that aniline manufacturers have not found it out long before. I shall describe it here but briefly, referring the reader to a more detailed account in *Dingler's Polytechnische Journal*, July 1867, vol. 185, p. 49.

Almost every aniline oil is produced by transforming benzol into nitro-benzol, and this latter into aniline. The benzols are all obtained from coal tar, and will therefore all contain substantially the same hydrocarbons, though in different proportions. We have seen before that every commercial benzol can be separated into a portion that boils between 80° and 100° , and another that boils between 100° and 130° C.; and that by dividing the benzol in this manner two liquids are obtained which yield by nitrification two sorts of nitro-benzol of very different smell and boiling points; these, again, yield two different anilines, commonly called light and heavy anilines. (I call these two sorts *Kuphaniline* and *Baraniline*, from *κοῦφος* light, and *βαρύς* heavy.) It is very easy to see that kuphaniline consists substantially of aniline, baraniline containing but a small quantity of this base, and therefore more toluidine. Both contain a small quantity of water, undecomposed benzol, and nitro-benzol. Of course these two sorts of aniline oil will begin to boil at very different temperatures, and a very different percentage of the two oils will distil when both are heated to the same temperature.

To render this difference clear, we may heat slowly a certain quantity of any sort of aniline oil—kuphaniline or baraniline—and notice well the quantities of the oils distilled at various temperatures, degree by degree. To simplify the operation, notice the quantities distilled during a rise of temperature amounting to 5° . As for practical purposes the difference between the specific weights of the two sorts of oil is of no importance, the quantities of distilled oil may be determined by receiving them in a graduated cylinder.

I put 100 cubic centimetres of kuphaniline in a glass retort, which I placed in a bath of oil or paraffin heated by a lamp. The tube of the retort was joined to a Liebig's condenser, and at the extremity of the condensing tube I

FIG. 5.



placed as receiver a graduated cylinder (*a*) by which the number of cubic centimetres of distillate could be observed. Of course the condensing apparatus was supplied with cold water. Having placed a thermometer in the neck of the retort, I began to heat.

At first some drops of liquid, consisting of benzol, a little aniline, and water distilled, so that when the mercury in the thermometer had risen to 180°C ., $8\frac{1}{2}$ cubic centimetres had distilled, of which $2\frac{1}{2}$ were water, and the rest a mixture of benzol with a little aniline and odorine. By continuing the heating the oil distilled in large quantities, so that when the thermometer had risen to 185° , 54 cubic centimetres had distilled between 180° and 185° . Up to 190° , 34 cubic centimetres distilled, so that the remaining oil was only $3\frac{1}{2}$ cubic centimetres. Of course another sample of kuphaniline oil will not yield precisely the same numbers, but they will be at all events similar to those above mentioned.

When baraniline is heated in the same manner up to 190° , from 100 cubic centimetres of the oil $3\frac{1}{2}$ will be distilled, of which 2 are water and the rest aniline oil, with a little undecomposed benzol. Between 190° and 195° , 8 cubic centimetres distil; then up to 200° , 18; from 200° to 205° , 39;

from 205° to 210° , 19; from 210° to 215° , 7 cubic centimetres; $5\frac{1}{2}$ remaining in the retort.

Now, if we compare the quantities of both oils distilled at different temperatures, we shall find a great difference; so that by distilling in the above manner it is absolutely impossible to mistake a kuphaniline for a baraniline, and *vice versa*.

Having thus investigated the different sorts of aniline oil by distillation, we must observe that every aniline oil can be considered as a mixture of kuphaniline and baraniline. Every aniline oil is produced from benzol, of which one portion can be distilled at a temperature of from 80° to 100° , and another quantity between 100° and 130° ; therefore every aniline oil is a mixture of kuph- and bar-aniline. It is easy to understand that we may produce, by mixing directly kuph- and bar-aniline, aniline oils of different boiling points. I have produced a series of these mixtures, and have found that every one differs from every other in the quantities of oil which will distil at different temperatures.

I have thus investigated several series of mixtures of kuphaniline and baraniline obtained by different operations, and have carefully noted the results. The mean results thus obtained I have drawn up in the form of a table.

Now it is quite clear that any aniline oil similar in its mode of distillation to any one of my artificial mixtures will be similar to it also in contents, and will be composed especially of the same quantities of kuph- and bar-aniline.

Of course this process will not enable us to recognise if an aniline oil contains one per cent of kuphaniline or baraniline, but such minutiae are of no consequence in practice. I have mixed the two kinds of aniline in such a manner that the proportions differ considerably, and have thus produced a table which enables any one to recognise the nature of every aniline oil found in commerce, and to produce by simple mixture from two sorts of aniline, useless for manufacture, another sort which yields very good results.

I have mixed—

90 per cent kuphaniline with 10 per cent baraniline.

85	„	15	„
80	„	20	„
75	„	25	„
$62\frac{1}{2}$	„	$37\frac{1}{2}$	„
60	„	40	„
50	„	50	„
$37\frac{1}{2}$	„	$62\frac{1}{2}$	„
25	„	75	„

By adding to the results thus obtained the numbers mentioned above, found by distilling pure kuphaniline and baraniline, I have constructed the following table:—

Deg. C.	100 K 0 B	90 K 10 B	85 K 15 B	80 K 20 B	75 K 25 B	$62\frac{1}{2}$ K $37\frac{1}{2}$ B	60 K 40 B	50 K 50 B	$37\frac{1}{2}$ K $62\frac{1}{2}$ B	25 K 75 B	100 K 100 B
180°	$2\frac{1}{2}$	7	$2\frac{1}{2}$	$5\frac{1}{2}$	$3\frac{1}{2}$	4	—	4	2	3	—
—	6	—	—	—	$3\frac{1}{2}$	3	—	3	2	$2\frac{1}{2}$	—
185°	54	50	$29\frac{1}{2}$	22	$5\frac{1}{2}$	$2\frac{1}{2}$	7	$4\frac{1}{2}$	—	$2\frac{1}{2}$	—
—	—	—	—	—	—	—	—	—	—	—	2
190°	34	34	$56\frac{1}{2}$	$55\frac{1}{2}$	$55\frac{1}{2}$	41	37	$7\frac{1}{2}$	$5\frac{1}{2}$	$4\frac{1}{2}$	$1\frac{1}{2}$
195°	—	5	$7\frac{1}{2}$	$8\frac{1}{2}$	15	25	33	42	40	17	8
200°	—	—	—	—	9	$8\frac{1}{2}$	—	19	$28\frac{1}{2}$	36	18
205°	—	—	—	—	$4\frac{1}{2}$	5	16	10	11	16	39
210°	—	—	—	—	—	$4\frac{1}{2}$	—	$3\frac{1}{2}$	$7\frac{1}{2}$	8	19
215°	—	—	—	—	—	—	—	—	—	$4\frac{1}{2}$	7
Residue	$3\frac{1}{2}$	4	4	$8\frac{1}{2}$	$3\frac{1}{2}$	$6\frac{1}{2}$	7	$6\frac{1}{2}$	$3\frac{1}{2}$	5	$5\frac{1}{2}$

In this way I distil every aniline oil whose nature I wish to study, and seek in the above table the series of results most similar to those obtained by the distillation. Thus the nature of any aniline oil can be ascertained as accurately as is necessary in practice in from a quarter to half an hour.

For manufacturing magenta an aniline oil of a certain composition must be used. Some aniline oils yield very good results, others very bad ones, and it was not possible formerly to discover whether a particular aniline oil could be used advantageously for this manufacture or not. I have investigated a great number of aniline oils which have yielded good results in various manufactories. On distillation I found them to be of similar composition to a mixture of 75 kuphaniline and 25 baraniline; hence we are led to conclude that this mixture is the most favourable to the manufacture

of magenta. But I shall speak of this subject again in another place.

I must here remark that by investigating kuphaniline and baraniline I have found the composition of the former to be 90 per cent aniline, 5 per cent toluidine, and 5 per cent odourine and water. Baraniline consists of 70 per cent toluidine and 30 per cent of the homologues of aniline and toluidine, which boil at a more elevated temperature.

This method of analysis, together with the details of my investigations respecting the determination of aniline oil, will be found in the above-mentioned page of *Dingler's Pol. Journal*.

We thus become acquainted with the true nature and composition of aniline oil, and are enabled to recognise in a short time the properties of any sample of this substance.

It will be useful here to add some remarks on the poisonous nature of aniline. Professor Letheby published some very remarkable notes on this subject which I cannot forbear mentioning. According to Letheby, aniline has a narcotic effect on the animal organism. Taken in doses of from 1 to 7 grammes it has a dyeing action on the organism. The features of the person who has taken the poison become bluish, the lips and jaw turn bluish grey, &c. The salts of aniline are much less poisonous than aniline itself. It has long been known that nitrobenzol is poisonous only because it becomes reduced to aniline in the stomach.

Aniline poisoning can easily be recognised as follows:—The contents of the stomach of the poisoned person are macerated with water containing a little sulphuric acid. The mass thus obtained is distilled, after mixing with an excess of potash solution. The distillate is carefully collected, and after the addition of a little sulphuric acid, is evaporated. If aniline be present, at the top of the solution where its level touches the vessel, a purple or red margin is found; 1-2000th grain of aniline can be well recognised in this manner by evaporating in a platinum vessel which is connected with the positive pole of a galvanic battery, the negative electrode

being in the fluid. The nascent oxygen at the positive pole oxidises the aniline present, and produces coloured compounds. It has often been observed by aniline manufacturers that the workmen not only suffer from the use of arsenic, but also from that of aniline, especially when they work in apartments where aniline vapours are mixed with steam.

CHAPTER IV.

MAGENTA.

ALTHOUGH not discovered first, it is preferable to begin with the red colouring matter derived from aniline.

In this chapter I shall describe the several methods of preparing a red dye from aniline, and I shall call these aniline reds *magenta*, because till now it was not proved that there was any other red aniline colour besides magenta.

As regards the aniline used in the manufacture of magenta, Hofmann* has proved that neither pure aniline nor pure toluidine are able to produce this colour, but only a mixture of both the above-mentioned bases. I shall speak on this subject again when I discuss the theory of the formation of aniline red.

I have already shown† that an aniline oil consisting of 75 per cent kuphaniline and 25 per cent baraniline may be best employed in the manufacture of aniline red. By this analysis of the two sorts of aniline oil we are able to determine the quantities of pure aniline and toluidine which will yield the largest quantity and the best quality of magenta, viz., a mixture of three parts of aniline with one part of toluidine, the other contents of aniline oil being indifferent as regards the manufacture of magenta.

* Comptes Rendus, part 56, p. 1062.

† DINGLER'S Pol. Journ., 1867, pp. 185, 189.

Of the transformation of this mixture into magenta we shall speak hereafter.

Magenta was first known under the name of *fuchsine*, which name is still general in France and Germany. The name is taken from the name of a flower having a colour very similar to magenta, the fuchsia codinea. From it fuchsiacine was at first formed, which was then soon abbreviated to fuchsine. The colour was introduced into commerce about the time of the battles of Magenta and Solferino; hence the name now most generally used to denote this bright bluish red colouring matter.

The red colouring matter was at first produced by treating aniline with anhydrous chlorides. Thus, A. W. Hofmann obtained a red colour from aniline by treating one part by volume of bichloride of carbon (CCl_2) with three parts of aniline, at 170° to 180° C., in a sealed tube for the space of 30 hours; a blackish mass was thus produced. Treated with water this substance was only partly dissolved, a considerable residue remaining. The solution yields with potash an oil-like precipitate containing much unaltered aniline. Freed from this by boiling with potash, the precipitate is transformed into a thick oil which gradually crystallises. Upon washing with cold alcohol, and crystallising from hot alcohol, this substance becomes quite white, whilst the solution is of a bright crimson colour. The portion of the above-mentioned mass insoluble in water can be easily dissolved in hydrochloric acid, from which solution alkalis precipitate a dirty red powder, soluble in alcohol with a crimson colour.

The white substance is said to have the formula $\text{C}_{38}\text{H}_{17}\text{N}_3$; it is a base soluble in all acids. The red coloured substance is said to be quite different from common magenta, and is usually called Hofmann's red, though I think that the difference between this substance and magenta depends only upon an unimportant admixture.

MM. Mounet and Dury, of Lyons,* have produced this red colour on a large scale. They heat one part of bichloride

* DINGLER'S Pol. Journ., 1861, vol. 159, p. 392.

of carbon with four parts of aniline in a copper vessel lined with lead, at a temperature of 116° — 118° C. To complete the operation the vessel is finally heated to 170° — 180° C.

Instead of bichloride of carbon, which Hofmann employed, M. Natanson* in 1856 used chloride of elayl to obtain a red colour from aniline.

On the 8th of April, 1859, a patent was granted to MM. Renard and Franc, of Lyons, for a method of obtaining magenta from aniline by means of bichloride of tin. The bichloride of tin employed is anhydrous, and is usually called *spiritus fumans libavii*. This substance is mixed with the aniline, and heated from 15 to 20 minutes to 180° — 200° C. The mixture becomes at first yellow, and then turns dark red. The mass thus obtained is poured while still warm and fluid into water, which is then boiled. All the undissolved substances are then allowed to precipitate, and the liquid is filtered. The solution now contains a hydrochlorate and a resinous substance. To obtain the colour pure some soluble salt is added to the mixture, whereby the colouring matter is precipitated, as magenta is very difficultly soluble in salt solutions.† Common salt, nitrate of potash, &c., are employed for this purpose.

To separate the adhering salts the precipitate is treated with a little cold water, and the colour is then dissolved in hot water and filtered. On cooling, the solution yields first a resinous precipitate, and then the colouring matter, which by crystallisation from alcohol can be obtained in small plates of a greenish metallic lustre.

The patent of MM. Renard and Franc includes not only bichloride of tin, but generally all chlorides, iodides, bromides, and fluorides of tin, mercury, and iron, together with the sulphates, nitrates, and chlorates of these metals. Hence the method of Mr. R. A. Brooman‡ to obtain magenta by treating aniline with anhydrous bichloride of mercury or titanium, or with bromide or iodide of tin, is already included

* Annal. d. Chem. u. Pharm., 1856, vol. 98, p. 291.

† We shall return to this subject again.

‡ Rep. of Pat. Inv., Aug. 1860, p. 112.

in the terms of the patent of Renard and Franc. In the same way, also, crystallised hydrated bichloride of tin can be used for the preparation of magenta.

A new method of getting the red colour was introduced by M. A. Schlumberger,* who in 1860 employed crystallised nitrate of the protoxide of mercury (Hg_2O , $\text{NO}_5 + 2\text{HO}$). To 100 parts of aniline he added 60 parts of the nitrate, and heated the mixture in a glass retort till it boiled. Magenta can be extracted from the resinous mass thus obtained by means of water, a brownish violet resin being left as a residue.

This method is included under the terms of the patent granted in 1859 to Thomas Perkin, who produced an aniline red by treating aniline with neutral or basic nitrate of the proto- and per-oxide of mercury, sulphate of the protoxide of mercury, and the nitrite of the same base. 10 parts of aniline were employed with from 6 to 8 parts of the basic nitrate of the protoxide of mercury, whereby a bluish red paste was obtained, metallic mercury falling down to the bottom of the vessel. By a similar process, M. Geber-Keller† produced magenta, called by him azaleine. According to the specification of this discoverer's patent, 10 parts of aniline are to be treated with 7 parts of dry powdered nitrate of peroxide of mercury. The heating is continued from 8 to 9 hours, at a temperature of 100° to 106° C. Aniline is thus transformed into magenta, while the mercury falls to the bottom. The mass thus obtained is allowed to cool, then boiled with water, and the solution allowed to crystallise. The magenta is obtained in splendid large octohedra, having a bright metallic lustre similar to that of the wing cases of cantharides.

This method of obtaining magenta is still employed in making the purest aniline red, which is known by the name of *rubine*. In the manufacture of this, aniline is treated with a neutral and quite concentrated solution of nitrate of peroxide of mercury, for from 10 to 18 hours, at a temperature of 120° C. In this way a thick red liquid is formed, mercury

* DINGLER'S polyt. Journ., vol. 157, p. 292.

† Reprt. d. Chem. Appl., 1860, ii., p. 52.

sinking to the bottom of the vessel. To separate the excess of aniline from this liquid (which cannot be distilled at 120°) the whole is poured into an iron retort, whence the aniline is distilled off by means of steam, and the red colour formed in the above operation is dissolved in the water. Common salt or sulphate of soda is then added to the solution, whereupon, after cooling, crystals of magenta are deposited, which may be purified by re-crystallisation.

At the low temperature at which this red colour is formed, it retains all its splendour and brightness, and at the same time a much smaller quantity of the resinous substance is produced. Moreover, the mercury being quite reduced, and completely separated from the mass, this kind of magenta is quite free from poison, and may be used by confectioners. It is much employed in dyeing silk. In manufacturing this colour, I observed that the nitrate of mercury must be entirely free from nitrous acid, which is formed when mercury is dissolved in nitric acid. For this reason it is better not to employ directly the solution of mercury in nitric acid, but to allow the solution to crystallise. The crystals are to be collected, dried, and stirred in a porcelain pan over an open fire until all the nitrous acid and excess of nitric acid are evaporated. Then the crystals are again dissolved in water, and the concentrated solution is employed to manufacture magenta.

The phosphate and acetate of mercury have been used by Mr. C. G. Williams,* to make magenta. The same chemist also uses arsenious acid for this purpose. He adds to 1 equivalent of hydrochlorate of aniline, 2 equivalents of water, and a mixture of 3 equivalents of aniline and 1 equivalent of arsenious acid. The colouring matter is produced on heating.

Nitrate of lead has been employed to make an aniline red, by MM. Dale and Caro.† Aniline is saturated with hydrochloric acid gas, and then heated for $1\frac{1}{2}$ hours in an oil bath at a temperature of 190° C.; the nitrate of lead is now

* London Journ. of Arts, Nov. 1863, p. 268. DINGLER'S Polyt. Journ., 170, 442.

† English Patent, granted May, 1860.

added as a dry powder with constant agitation. The colouring matter thus obtained is dissolved in boiling water, and precipitated by nitrate of soda, common salt not being adapted to this purpose, because chloride of lead is almost insoluble in water.

MM. Depouilly and Lauth oxidise aniline in the most direct way. They use instead of nitrates, nitric acid itself. Their patent is dated June, 1860, and according to the specification nitrate of aniline is heated to 200° C. To prevent a too violent reaction of the nitric acid on aniline the latter must be employed in excess.

Mr. E. J. Hughes, whose patent is dated January, 1860, heats aniline and nitric acid directly in a retort. A mixture of 32.5 parts of nitric acid of specific gravity 1.36, and 100 parts of aniline, are heated in a retort to 150° or 200° C. All the water of the nitric acid being distilled off, the residue in the retort is boiled one hour, whereby a thick dark red syrup-like mass is obtained. The substance is then treated with a solution of carbonate of soda until it is quite neutral; 20 parts of pure water are boiled, and 1 part of the mass thus obtained is added; the heating is then continued until all the resin has risen to the top and is taken off. By filtering and allowing to cool, the solution yields a red coloured mass having a metallic green reflection, which is ground and sold direct.

Mr. Blackley, and afterwards Mr. Watson, have proved that it is possible to obtain magenta as a violet and blue colour by treating aniline with aqua regia (chloro-nitrous acid, NO_2Cl).

None of the methods we have hitherto spoken of are now employed in practice, having been superseded by a method that especially excels in the cheapness of the materials used in the reactions. The process of preparing magenta by means of nitrate of mercury is, however, still used in some cases, but its employment is very limited, and I know only two manufactories where it is practically effected.

Magenta is now only made by treating aniline with arsenic acid (AsO_5). In January, 1860, an English patent was

granted to Mr. H. Medlock for obtaining magenta, as follows:—2 parts of aniline are mixed with 1 part of dry arsenic acid, and left either at common temperature or the boiling point of aniline, until the mixture has acquired a deep purple colour. The solution of this mass in water is filtered, whereupon a purple tarry colouring matter is left on the filter, which can be dissolved by treating with alcohol. This patent specification has the same peculiarity common to a thousand others: it cannot be carried out in practice. We shall show hereafter that only a solution of arsenic acid is able to transform aniline into magenta. Moreover, the method of purifying the mass obtained is wholly insufficient, so that it is impossible to get a useful colour by following Mr. Medlock's patent specification.

A second patent, for France, founded on the employment of arsenic acid, was granted to MM. C. Girard and G. de Laire,* in Paris.

A solution of 12 parts of arsenic acid in 12 parts of water, is mixed with 10 parts of aniline oil and raised to 120° C. At the end of the operation the temperature is raised to 160° C., which degree must be never exceeded. After from 4 to 5 hours the operation is finished. Thus a homogeneous mass is formed, which liquefies under 100° C. Allowed to cool, this solidifies and takes a bright metallic lustre. It is easily soluble in water, the colour of the solution being red.

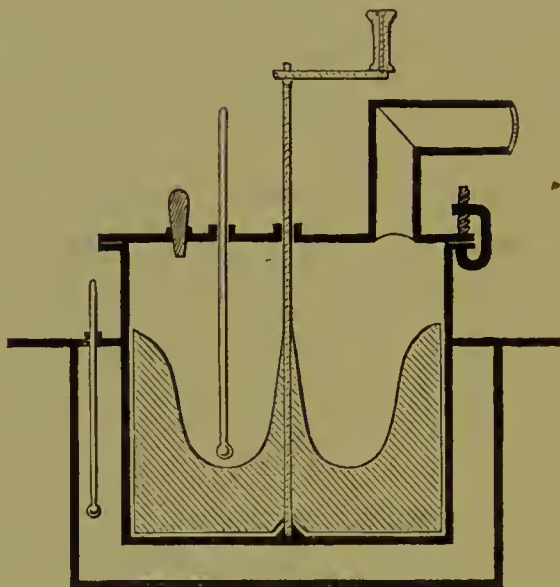
These are the principles on which the manufacture of aniline red or magenta is founded. The employment of arsenic acid and aniline is the same throughout; the subsequent treatment alone being variable.

We will describe here the apparatus used for making magenta. For the purpose of treating aniline oil and arsenic acid dissolved in water, a vessel is used of the form of an iron pot, enamelled in the inside, and closed with a lid, through which an iron agitator reaches into the apparatus. In the lid is also an opening through which a thermometer may be introduced into the liquefied mass, and another

* DINGLER'S Polyt. Journ., vol. 159, p. 229, 452.

closed with a wooden stopper through which the progress of the operation may be observed. A third opening in the lid admits an iron tube bent at a right angle, which can be joined by an india-rubber tube to a condensing apparatus, so as to collect the aniline which is vapourised during the

FIG. 6.



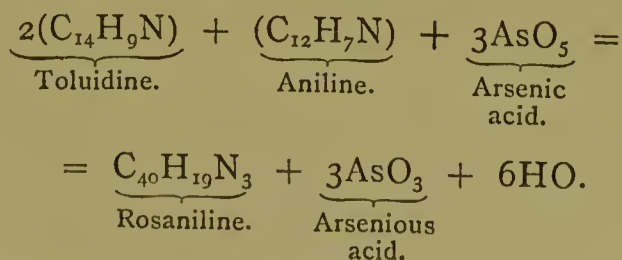
operation. The lid is movable, fastened with screws, and tightened with a lead washer. The whole apparatus, the capacity of which varies according to the quantities dealt with, is surrounded with another pot of the same form, and the latter is filled with glycerin or paraffin. A thermometer is also put in the surrounding vessel to observe the temperature there. The second vessel is heated over an open fire, and serves only as an oil bath.

The inner vessel is filled with 100 parts of aniline oil, and 150 to 200 parts of a solution of arsenic acid, containing 75 per cent of the dry acid. After removing the lid of the vessel, aniline oil is first poured in, then the dissolved arsenic acid is gradually added. As soon as aniline and arsenic acid are mixed, heat is produced, and a white or reddish mass is formed consisting of arseniate of aniline. When all the arsenic acid has been added, the lid is fastened down and the agitator is moved. The oil bath is heated, and the arseniate of aniline now liquefies and assumes a reddish colour. The heat is then raised to $180^{\circ}\text{C}.$,

the temperature at which aniline oil begins to boil. (Of course the thermometer in the outward vessel must stand at about 185° in order that the inner vessel may be at 180° .) Aniline and water now distil through the bent pipe into the condensing tube, and are collected in a receiver. The mass in the vessel gradually becomes thicker, and finally so thick that the agitator can only be moved with difficulty. From time to time an iron rod is introduced, by removing the wooden stopper from the hole in the lid. The small portion of the mass adhering to the rod is removed and allowed to cool; if its colour after cooling is of a pure metallic bronze, the mass is fit for use. If the colour is still blackish the mass must be left some time longer in the vessel.

During the whole operation the agitator must be constantly turned to prevent the contents from adhering to the walls of the vessel. When the mass is ready it is taken out of the vessel by means of a large iron spoon. The workmen employed in this work must guard against the poisonous vapours, by binding a cloth over the mouth and nose. The liquid mass is put into a wooden box lined with paper, where it is allowed to cool. After cooling, the mass takes a greenish metallic lustre, which is brighter as the operation is more successful. It finally becomes so hard as to require to be broken with a hammer into small pieces.

We have before shown that by mixing aniline with a solution of arsenic acid, arseniate of aniline is formed, but by heating, this is again transformed into another substance. The arsenic acid oxidises the mixture of aniline and toluidine contained in the aniline oil, to a red substance called by chemists *rosaniline*, being transformed and becoming arsenious acid (AsO_3), so that we may represent the whole process which takes place in the vessel by the formula—



The basic rosaniline combines with the excess of arsenic acid contained in the mass, and forms arseniate of rosaniline. The excess of aniline oil and the water from the solution of arsenic acid, together with that formed during the process, volatilise and are collected in the receiver.

In this operation not only rosaniline—the basis of magenta—but also a number of other basic substances are formed, of which we shall speak hereafter. It is therefore impossible for the transformation of aniline into rosaniline to be as simple as represented by Hofmann in the formula given above.

The time occupied in the operation is not always the same. It depends on whether the aniline oil contains an excess of toluidine or of aniline. In the former case the process will last longer than in the latter. The aniline oil best for making magenta is, as above mentioned, that containing 75 per cent kuphaniline and 25 per cent baraniline. All other mixtures will yield rosaniline, but not so quickly or of so good a quality.

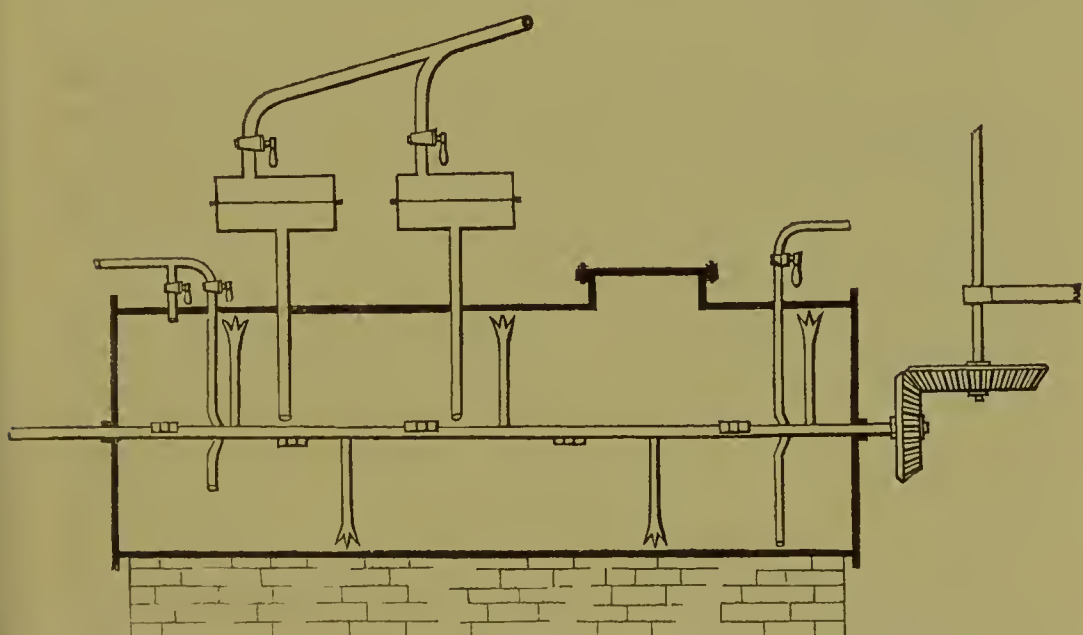
The molten mass produced as above mentioned is broken into pieces with a hammer and heated with boiling water. This was formerly effected by putting the pieces into a vat and pouring water on them, steam being introduced through a tube to cause the water to boil. The boiling water dissolves the red base combined with arsenic acid, a brown tarry mass remaining. In order to dissolve out all the red colour included in the tarry mass, the crude colour, liquefied by the heat of boiling water, must be well stirred up with poles by the workmen. When the water is saturated with the colour it must be drawn off and filtered, fresh water being poured on to the molten mass until no more red is contained therein, and the solutions must be filtered to separate the portions of resinous substances mechanically mixed with them. For this purpose a filter of felt or cloth was formerly employed, but this being soon obstructed by the resinous mass, an immense quantity of filtering material was necessary to filter an inconsiderable quantity of the solution. The solution also was formerly

ladled from the vats into the filters. This caused much to be spilt, so that the floor of the manufactory was always covered with the red fluid.

All these inconveniences may be prevented by using the apparatus now about to be described. It is not yet generally known, and in many manufactories they still work by the old imperfect method.

The molten mass is put into a boiler, such as is used for steam engines. This boiler, of a simple cylindrical form, bears a shaft turning in the middle of the boiler by means of

FIG. 7.



suitably arranged machinery. The shaft carries iron paddles on every side, which when it turns, work in the liquefied mass. Upon this, water is poured through a tube and is heated by steam introduced through another tube which reaches almost to the bottom of the boiler.

While the water boils the temperature is kept up by the introduction of fresh steam, and the claws work upon the colour mass, causing every portion of it to come into contact with the boiling water. When this is saturated, it must be drawn off and filtered, which two operations are thus effected at once. A tube reaches almost to the bottom of the

boiler, and the tap being opened, the solution is forced by means of steam through this tube, and led by it into the crystallising vats. As it leaves the boiler the solution is made to pass through a filter. This consists of two shell-shaped iron vessels screwed closely together. Between them is a felt plate through which the solution is pressed by means of steam from below upwards. The resinous substances in the solution cannot pass the felt, and are retained at its surface, but being hot they drop down again into the boiler and do not clog the filter. When one filter is clogged another can be substituted by closing one and opening the other tap. The filter is then taken out, and the felt cleaned or replaced by a fresh piece.

Thus, without any inconvenience, the solution of aniline red is brought to any part of the manufactory, and filtered at the same time, all waste of the red liquid being entirely prevented. The solution when put into the crystallising vats is mixed with from 2 to 4 per cent of common salt, for two purposes:—First, to transform the arseniate of the red base into the hydrochlorate, then to precipitate this hydrochlorate, the salts of the red base being difficultly soluble in solutions of other salts. After two or three days the walls of the vat are found covered with crystals of magenta, whereupon the solution is drawn off and employed, instead of a fresh supply of water, to extract another quantity of crude magenta mass.

The crystals obtained, as above described, are re-dissolved in pure water to form a hot concentrated solution, and treated once more with common salt. A purer magenta is now obtained, which, after crystallisation for the third time, will be found quite pure and of a splendid shade.

In high vats larger crystals are obtained than in low vessels. Very large crystals are also obtained by allowing the liquid to cool very slowly, and also by using sulphate of soda in the place of common salt. Then the sulphates of the red bases are formed, which produces larger crystals containing a smaller proportion of the base than those of the hydrochlorate. Such large crystals are sometimes produced, and are usually sold under the name of Diamond Magenta.

The remaining solutions contain arseniate and arsenite of soda, and are therefore exceedingly poisonous. To free them from arsenic they are mixed with milk of lime, whereby arseniate and arsenite of lime are precipitated, together with a little colouring matter still contained in the solution. It is, however, best to evaporate the whole solution in large iron pans under a chimney with a strong draught, whereby the arseniate of soda is obtained in beautiful crystals, which may be used in calico printing, &c.

A larger quantity of magenta may be obtained from the solutions by adding crystals of soda when magenta ceases to be produced by evaporation. A considerable additional quantity of colouring matter may thus be obtained, which is redissolved and added to any crystallising solution.

In a well conducted operation 34 lbs. of magenta may be produced from one to two cwts. of aniline oil, provided that the aniline oil used is of suitable composition.

Formerly the crude red colour mass was extracted by dilute hydrochloric acid, and then precipitated by carbonate of soda or caustic soda. This method, however, was found in practice so inconvenient that it has been entirely abandoned.

In 1860 Mr. R. Smith, of Glasgow, took out a patent for the transformation of aniline oil into magenta. The operation described by Mr. Smith* is very long and inconvenient, and, what is worse, useful magenta cannot be obtained by this method; it is therefore of no value.

Nitrate of antimony ($2\text{SbO}_3, \text{NO}_5$) has even been used for making magenta. Mr. Gratrix mixes five parts of aniline oil with four parts of the nitrate (got by adding fuming nitric acid to protoxide of antimony) and heats the mixture to 82°C .; the liquid part of the mass is then separated and heated for ten minutes to 177°C . The red colour thus obtained is extracted in the usual manner.

In this method the antimony does not seem to be of any importance. Its nitrate being a very weak compound, the

* Polyt. Centrabl., 1864, p. 754.

protoxide is immediately set free, and the nitric acid transforms the aniline oil into magenta. Even water when added to the nitrate of antimony decomposes it; this operation is, therefore, in fact identical with that of Mr. E. J. Hughes, mentioned above.

To complete these remarks we will still mention some methods of transforming aniline into magenta, which are of no importance in practice.

Bran, flour, saw-dust, &c., distilled with half their weight of sulphuric acid and the same quantity of water, yield an acidulous distillate, which, after saturation with potash and re-distillation, yields water and a few drops of an oil which can be separated by chloride of calcium.

This oil is called furfurol. Its empiric formula is $C_{10}H_4O_4$. It is colourless, becomes brown by exposure to the air, and boils at $163^{\circ}C$. It is soluble in water, spirits, and ether. Mr. Stenhouse* obtained a beautiful red colour by treating aniline with the above-mentioned furfurol. He isolated the red colouring matter by allowing the solution of acetate of aniline and furfurol to stand at rest.

A pitch-like substance covers the walls of the vessel, the solution becoming colourless. This pitch-like substance is the pure colouring matter, and has a surface lustre similar to that of the wing scales of cantharides. It is insoluble in water, and may be dissolved in spirits, methyl alcohol, and acetic acid. Wool and silk dyed with this substance to a red shade similar to magenta are, however, bleached again after a few hours' exposure to the air, even if the dyed substances are not submitted to the influence of light.

The method of making magenta invented by M. F. Folt† is very interesting. This chemist uses the oxygen of indigo, which is transformed by every reducing agent into white indigo.

M. Kœchlin‡ prepares a substance similar to magenta by treating aniline oil with crude wood vinegar, or wood tar.

* *Repert de Chimie Appl.*, ii., p. 220.

† *Ibid.*, 1892. *DINGLER'S Polyt. Journ.*, 165, 397.

‡ *Ibid.*, Sept., June, 1859, p. 404.

Here the empyreuma of these substances undoubtedly produces the effect.

In 1860, Mr. Smith showed that magenta might be formed by heating aniline oil with iodine or iodide of mercury.

G. Delvaux heats a mixture of one equivalent of aniline with one equivalent of the hydrochlorate of aniline for from six to eight hours, at a temperature of about 150°C . A certain quantity of magenta is thereby formed, which may be extracted by means of water. To simplify the process two equivalents of aniline and one equivalent of hydrochloric acid may be used. Magenta is then obtained by heating and evaporating the water from the solution.

Every aniline salt yields magenta when heated with pure aniline to 150°C . Sulphate of aniline heated to 200°C ., turns to a violet black, and then yields, when treated with water, a solution of magenta. In a similar manner, hydrochlorate of aniline is transformed into a red colour, by heating it dry and mixed with sand or fluor spar, for three hours to a temperature of 180°C .

To produce magenta in this manner on a large scale, according to M. Delvaux, one equivalent of hydrochlorate of aniline is mixed with tenfold its weight of sand, and one equivalent of aniline. After agitation, the mixture is heated for fifteen hours, at from 110° to 120°C ., or five to six hours to 150° , or two to three hours to 180° . The mass so treated is then put into boiling water, by which a large quantity of the red colour is dissolved out.

Theoretical Observations on Magenta.

The investigations into the theoretical composition of magenta arose out of a patent suit between the discoverer of *azaleine*, Geber-Keller, and the firm Renard and Franc, of Lyons, the manufacturers of the so-called *fuchsine*.

In this suit the authorities on the subject of the chemistry of colours gave their judgments; these were very different, and have now only an historical interest; none of the pro-

posed views of the composition of magenta possessed any probability. This was owing to the fact that the investigations had hitherto been made upon impure magenta, while no one suspected the presence of any impurity. Thus M. A. Béchamp,* MM. Persoz, de Luynes and Salvétat,† MM. Bolley, Guignet, Geber-Keller, Williams, Schulz, Kopp,‡ Jacquemin, and others investigated magenta, and deduced formulæ entirely differing among themselves.

Finally, Dr. Hofmann settled the composition of magenta through his classical investigations upon rosaniline. Dr. Hofmann|| has proved that the cause of the different results obtained by the above named chemists, is that they worked with impure products, and he comes to the conclusion that the two colouring matters, which caused so much investigation, had only an inconsiderable difference, the azaleine of M. Geber-Keller being the nitrate, and the so-called fuchsine of MM. Renard and Franc the hydrochlorate of the same base, called by Hofmann rosaniline.

In his investigations, Dr. Hofmann used materials supplied him by the great London firm, Messrs. Simpson, Maule, and Nicholson, who sold magenta under the name of roseine. He found that this colouring matter was the acetate of an organic base, which he called rosaniline. The boiling aqueous solution of this salt yielded, when mixed with ammonia, a crystalline precipitate of a reddish colour, which was the new base in a tolerably pure state. The solution separated by filtering this precipitate contains the base in a still greater state of purity; it may be obtained by allowing the filtered solution to cool. The perfectly pure base is thus obtained in the form of colourless crystalline needles and plates. But the solubility of this substance in ammoniacal water is so slight, that only small quantities can be thus obtained. It is more easily soluble in alcohol, which it colours red, but is quite insoluble in ether. In the atmosphere the base turns at first reddish, and finally dark red.

* DINGLER'S Polyt. Journ., vol. 156, p. 309.

† DINGLER, vol. 159, p. 221.

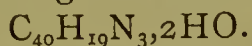
‡ Chem. Centralbl., 1861, No. 34.

|| DINGLER, vol. 165, p. 60.

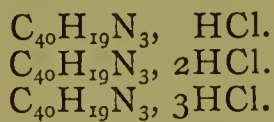
This variation of colour is said to be unaccompanied by a variation in weight.

At 100° C. rosaniline quickly loses a small quantity of adhering water; the heat may then be continued up to 130° without any variation in weight.

At a high temperature the base is decomposed, a coke-like mass remaining, and an oil distilling which consists principally of aniline. According to his analysis Dr. Hofmann thought that the formula of rosaniline was $C_{40}H_{21}N_3O_2$, which he changed after analysing the salts of the base into



Rosaniline is a well characterised base yielding several series of readily crystallised salts. Dr. Hofmann finds that it forms three series of salts, the hydrochlorates being of the formulæ—



The salts containing one equivalent of acid and base are most easily formed, and may be obtained again on recrystallisation. Those containing three equivalents of the acid are decomposed both by water and by a temperature of 100° C.

The several salts of this colour base may be obtained by direct addition of the proper proportion of acid. The salts containing one equivalent of acid exhibit by reflected light a bright metallic lustre, similar to that of the wing covers of cantharides. In transmitted light they appear red, and when in thick layers are opaque.

The salts containing three equivalents of acid are of a yellowish brown colour, both in a solid form and when dissolved. They are more soluble than those with one equivalent of the acid. Both series of salts crystallise easily.

The hydrochlorate of rosaniline, $C_{40}H_{19}N_3, HCl$, is obtained from its boiling solution in well characterised starlike rhombic plates. It is difficultly soluble in water, more easily in alcohol, and insoluble in ether.

At 130° C, it gives off all accompanying water. At 100°

it retains a little, and, like most rosaniline salts, is very hygroscopic. It is more soluble in dilute hydrochloric acid than in water. The moderately heated solution of the hydrochlorate of rosaniline, when mixed with concentrated hydrochloric acid, solidifies on cooling to a magma of bright brown needles, which when washed with concentrated hydrochloric acid, and dried in vacuo over sulphuric acid, have the formula $C_{40}H_{19}N_3, 3HCl$.

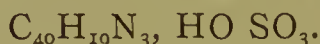
At 100° C. this hydrochlorate gradually loses its acid, and turns indigo-blue; upon continuing the heat of 100° the colour becomes red, and the salt is re-transformed into the hydrochlorate with one equivalent of acid. It is probable that the change of colour into blue is due to the formation of a hydrochlorate containing two equivalents of acid.

Both the hydrochlorates investigated by Dr. Hofmann combine with chloride of platinum to form double salts, the composition of which is said to answer to the formulæ—



The hydrobromate of rosaniline is in all respects similar to the hydrochlorate, but is still less soluble. When dried at 130° it has the composition $C_{40}H_{19}N_3, HBr$.

The sulphate of rosaniline is obtained by dissolving the pure base in dilute sulphuric acid. When the solution cools, crystals of a salt are formed, which has the formula—



This salt is with difficulty soluble in water, more easily in alcohol, but is quite insoluble in ether. There is also another acid sulphate which was not investigated.

In the same manner the oxalate of rosaniline may be obtained. When dried at 100° its formula is—



It is very difficult to free this salt from its water of crystallisation, the temperature at which it loses its water being very near to that at which it is decomposed.

The acetate, of the formula $C_{40}H_{19}N_3, HO C_4H_3O_3$, is, according to Dr. Hofmann, the most beautiful of the whole series. Nicholson obtained it in crystals half an inch in

thickness. It is easily soluble both in water and in alcohol, on which account it is difficult to crystallise it.

The formiate is similar to the acetate.

The chromate of rosaniline may be obtained by adding a solution of bichromate of potash to the acetate of rosaniline dissolved in water. A brick-red precipitate appears, which is transformed by boiling water into a green, crystalline, almost insoluble powder.

The picrate crystallises in beautiful red needles, which are only with difficulty soluble in water.

Rosaniline is altered by reducing agents, especially by hydrogen and hydrosulphuric acid.

A solution of rosaniline in hydrochloric acid is soon decolorised on the addition of zinc. The liquid then contains, besides chloride of zinc, the hydrochlorate of a new base, which both when pure and when combined with acids, is quite colourless. This base Dr. Hofmann called leukaniline. It was obtained from commercial magenta, and by repeated purification is obtained of a yellow colour. The pure base, though quite white, easily turns reddish on exposure to the atmosphere. It is scarcely soluble in cold, but somewhat so in hot water, and on cooling is deposited by the solution in small crystals. Alcohol dissolves the base abundantly, but ether only in very small quantities. The best solvent for leukaniline seems to be a solution of the hydrochlorate of leukaniline, in which it dissolves in large quantities, and can be obtained again in the form of needles. It may be dried in vacuo over sulphuric acid without variation of colour. When heated cautiously, it turns red, and liquefies at 100° , forming a dark red fluid, which solidifies on cooling to a mass not so richly coloured. It contains no water, and answers when dried at 100° to the formula $C_{40}H_{21}N_3$. This formula was found to be correct by the analysis of the hydrochlorate, chloro-platinate, and nitrate.

The hydrochlorate may be obtained as follows from common magenta:—

The magenta—hydrochlorate of rosaniline—is transformed by treating it with hydrosulphate of ammonia, as above described in the case of leukaniline. The yellow mass thus

obtained is powdered, and freed by means of water from the adhering hydrosulphate of ammonia, after which it is dissolved in diluted hydrochloric acid. The dark brown solution thus formed yields, when mixed with concentrated hydrochloric acid, an abundant crystalline precipitate, brown or yellow, according to the purity of the magenta employed. It may be purified by washing with concentrated hydrochloric acid, in which the precipitate is almost insoluble, but in most cases it is necessary to re-dissolve and re-precipitate it as above described. Before adding concentrated hydrochloric acid for the last time, the solution is heated to boiling, whereby on cooling the hydrochlorate of leukaniline crystallises in well formed rectangular plates, very small, but brilliantly white. By re-crystallisation in water the purifying is completed.

The hydrochlorate thus obtained, contains three equivalents of acid, and even when dried in vacuo, two equivalents of water. The formula is $C_{40}H_{21}N_3, 3HCl + 2HO$.

It cannot be completely dried in the atmosphere, but all the water may be separated by heating the salt for a sufficient time to $100^\circ C.$, and exposing to a current of hydrogen. It is not possible to obtain compounds containing a smaller proportion of acid by dissolving pure leukaniline in the solution of the hydrochlorate. If chloride of platinum is added to a moderately concentrated warm solution of the hydrochlorate of leukaniline, the liquid yields, on cooling, well-defined bright orange prisms, which are slightly soluble in cold, but decomposed in boiling water. When dried at $100^\circ C.$ they still contain two equivalents of water, which may be driven off at a higher temperature. The composition of the platinum compound is—

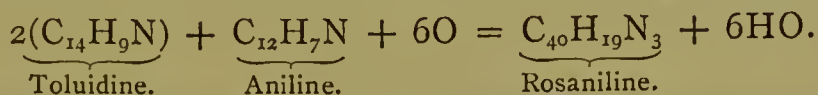


The nitrate crystallises in well-defined white needles, soluble in water and alcohol, insoluble in ether, and with difficulty in nitric acid. When dried in vacuo, they have the composition $C_{40}H_{21}N_3, HO NO_5 + 2HO NO_5 + 2HO$. The water of crystallisation cannot be separated, as the salt decomposes at 100° .

Leukaniline may be re-transformed by oxidising agents

into rosaniline. The two bases are therefore similar to blue and white indigo.

As to the formation of rosaniline from aniline oil, we have no precise information. It is only hypothetical to say that rosaniline ($C_{40}H_{19}N_3$) is formed by the addition of two equivalents of toluidine to one of aniline, six equivalents of hydrogen being oxidised by the oxygen of the arsenic acid:—

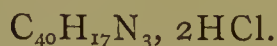


As before mentioned in the chapter on Aniline, the aniline oil best for manufacturing magenta is composed of one part of toluidine with three parts of aniline, so that five parts of aniline must be eliminated if one part of aniline combines with two parts of toluidine to form rosaniline. The formation of rosaniline, however, is not unconnected with that of other products. We have shown that when rosaniline is manufactured, the above mentioned brown resinous substance is also obtained. From these Mr. Ed. C. Nicholson extracted a new base of a yellow colour, which Dr. Hofmann* investigated. It is a fine yellow powder, similar to chromate of lead, scarcely soluble in water, but easily dissolved by alcohol and ether. It is a well characterised organic base, which, forming two series of well crystallised salts, has received the name of chrysaniline, on account of its yellow colour. For analysis the base precipitated from the mononitrate was employed. After dissolving and re-crystallising this salt six times, it was precipitated by ammonia, and the pure base thus obtained was analysed. When dried at 100°C. its formula was found to be $C_{40}H_{17}N_3$, and this was confirmed by the analysis of several of its salts. As will be seen, this base only differs from rosaniline by the subtraction of two equivalents of hydrogen.

The hydrochlorate of chrysaniline is easily obtained by adding concentrated hydrochloric acid to a solution of chrysaniline in dilute hydrochloric acid. It is obtained in this

* Compt. Rend., part 45, p. 818; DINGLER'S Polyt. Journ., 168, p. 133; Journ. f. Chem. u. Pharm., 1863, p. 33.

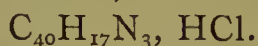
manner as a scarlet crystalline precipitate, consisting of small plates very soluble in water, less so in alcohol, and quite insoluble in ether. The formula of this salt is—



It sometimes contains water, and its formula is then—



When heated for a fortnight, at a temperature of between 160° and 180° , it is transformed into a yellow crystalline powder, less soluble in water, which has the formula—



The nitrates of chrysaniline crystallise very easily in ruby coloured needles insoluble in water. The other salts of chrysaniline are precipitated on the addition of any soluble nitrate, so that chrysaniline may be used as a reagent for nitric acid. When dilute nitric acid is boiled with an excess of chrysaniline, the mono-nitrate of this base is formed, which when the liquid cools crystallises in needles. Its formula is $\text{C}_{40}\text{H}_{17}\text{N}_3, \text{HO NO}_5$. By adding a solution of this salt to cold concentrated nitric acid a precipitate is formed of the formula $\text{C}_{40}\text{H}_{17}\text{N}_3, \text{HO NO}_5 + \text{HO NO}_5$, which can be obtained in well formed prisms. By re-crystallisation from water it loses its excess of nitric acid.

The very soluble sulphate is scarcely crystallisable.

Until lately it was not possible to reproduce rosaniline from chrysaniline. Even the formation and constitution of this substance have only recently been known.

The salts of this base are used as an orange dye.*

The existence of this base plainly shows how it is that magenta is sometimes obtained of a yellow shade, in which case a portion of the resinous base is contained in the red colour.

* See Chapter on Aniline Yellow.

CHAPTER V.

ANILINE BLUE AND VIOLET.

EVEN before the discovery of aniline red, violet shades were produced by treating aniline oil with certain agents, and soon after the discovery of magenta blue shades were obtained.

We may regard the violet, with the exception of one kind, to be an intermediate stage of the formation of aniline blue from the red colouring matter, that is to say, as an aniline blue the formation of which has been interrupted before the close of the operation, and in which therefore the substitution about to be described has been only incompletely effected.

It is indifferent whether we treat magenta with aniline oil or transform aniline oil at first into magenta, and then form aniline blue or violet by means of the excess of aniline. Generally it may be said that blue and violet are formed by treating magenta with reducing agents, or by adding oxidising substances to aniline oil. Hence it is as well to speak of the violet and blue in the same chapter.

All methods of obtaining violet immediately from aniline oil are now of only historical interest. We shall enumerate them in chronological order, but occupy ourselves only with those that are really in use, and which are all founded upon the production of violet and blue from magenta.

A violet, the first of all the aniline colours, was discovered by Messrs. Perkin and Church. They took out an English patent in 1858 for a method of producing a violet colour by

heating sulphate of aniline, toluidine, cumidine, or cymidine with bichromate of potash. A solution of one equivalent of sulphate of aniline is mixed with one equivalent of bichromate of potash dissolved in water, agitated, and left to stand. A precipitate is thereby formed, which is collected, washed with water to eliminate the sulphate of potash formed during the process, and then treated with fluid hydrocarbons to dissolve out a brown resinous substance which adheres to the colour. The mass thus treated represents the colour, which may be dissolved in alcohol or methyl spirit, and used at once for dyeing. Another method of purifying this colouring matter was proposed by M. Wilm* in 1861.

It was soon after discovered that these violets were strongly affected by oxidising agents, such as chloric acid, chromates, bleaching powder, &c., and by them changed to a blue colour. Acting on this discovery, M. H. Kœchlin,† of Glasgow, succeeded in transforming aniline directly into the blue colour. He heated one litre of aniline with $1\frac{1}{2}$ to 2 litres of hydrochloric acid and 80 grammes of bichromate of potash, at the temperature of the boiling point of aniline. He then saturated the liquid with a solution of hydrate of lime, and filtered. In this manner was obtained a blue solution having an alkaline reaction.

M. Fritsche‡ found as early as 1843 that aniline could be transformed into a blue colour by chlorate of potash.

To get the pure colouring matter Dr. Hofmann proposes to add a few drops of chlorous acid (ClO_3) to a solution of aniline in hydrochloric acid, whereby a blue mass is produced.

M. Béchamp|| obtains aniline blue by treating aniline with chlorine until a dark brown mass is formed, which he heats successively to a temperature of 180° and 200° C., whereby the brown mass is transformed into the blue colour. In a similar manner a blue colouring matter may be obtained by mixing a solution of the nitrate of aniline in water with powdered chlorate of potash, and adding to this mixture a strong

* Chem. Centralbl., 1861, No. 5, p. 69.

† Rep. d. Chim. App., 1860, p. 196.

‡ ERDMANN'S Jour. f. prac. Chem., 1843, vol. 28, p. 202.

|| Comptes Rendus, 1861, part 52, p. 538.

acid, such as hydrochloric, nitric, or oxalic, and a little sugar. Eight hours afterwards an abundant dark precipitate may be observed, which is collected, washed with water containing ammonia, and then dried. This is the pure blue; it possesses considerable dyeing power.

Crossley obtains a solution which dyes purple immediately, by cautiously heating an alcoholic solution of aniline and bisulphide of carbon with nitric acid. At the same time a resinous mass is formed from which Crossley obtains a yellow colouring matter.

According to Messrs. Beale and Kirkham, a violet may be obtained when one part by measure of an aqueous solution of hydrochlorate of aniline of the specific gravity of 1.01 is mixed with the same quantity of acetic acid (containing 25 per cent of the anhydrous acid), and there is added gradually a solution of bleaching powder of the specific gravity of 1.5 (Beaumé). By adding the solution of bleaching powder successively in small portions every shade of violet is easily obtained, and the more of the solution that is used the bluer will be the resulting shade. By an excess of bleaching powder the liquid is completely decolorised. A violet precipitate is formed, which is collected and heated with an alkali to eliminate the adhering resin. The violet itself is, like every aniline violet, quite insoluble in alkalis.

The colouring matter when prepared is dissolved in alcohol, and on evaporation is left in the form of green scales of a metallic lustre. The same result may be obtained by using a solution of chlorine in water. Almost the same method was patented in England by Messrs. Depouilly and Lauth in June, 1860.

Mr. George Phillips, on December 30th, 1863, patented a similar method, differing from the former only by moderating the action of the bleaching powder. He produces violet by adding 300 parts of sulphate of iron to 100 parts of sulphate of aniline and 40 parts of bleaching powder. The mixture is heated at 100° C. until the desired shade is obtained; the colour thus obtained is soluble in water, and may be obtained from its solution by precipitation in the ordinary manner.

Finally, the method of M. Béchamp* is interesting. He obtained a beautiful blue colour by mixing an equal number of equivalents of aniline and of phenic acid with water, and adding to this mixture an aqueous solution of bleaching powder.

A great number of oxidising agents have been proposed for the transformation of aniline into blue and violet. C. G. Williams, according to his patent of 1859, mixes a solution of 100 parts of sulphate of aniline with a solution of 112 parts of permanganate of potash. He then heats and obtains a precipitate containing a violet colouring matter. To eliminate the resin the precipitate is treated with benzol, and the colouring matter is dissolved in alcohol. Even peroxide of manganese produces a violet colour when an acid is present. On this circumstance is founded a patent dated May, 1859, and taken out by Mr. R. D. Kay. Mr. Price† substitutes oxide of lead for the peroxide of manganese.

According to a patent granted May, 1860, to Messrs. Dale and Caro, an aqueous solution of chloride of copper produces a violet when mixed with sulphate of aniline. In a similar manner Messrs. Persoz, de Luynes, and Salvétat produced a blue colour by heating an excess of aniline in a sealed tube with chloride of tin. This product was formerly sold as *Bleu de Paris*. The same result may be obtained, according to Mr. J. J. Coleman, by means of chloride of antimony. Mr. Städeler, of Zurich, found that aniline yielded violet colours when heated in a sealed tube with azobenzol, nitrobenzol, hydroazobenzol, &c.

We shall now proceed to describe those methods which are founded on the principle of heating aniline red or magenta with agents which transform it into violet or blue; in all of them the existence of magenta is pre-supposed.

MM. Schäffer and Gros-Renard employed a solution of shellac in any alkali to transform magenta into a blue colouring matter, called by the inventors *Bleu de Mulhouse*. Mr. E. Kopp,‡ who describes this method, says that a solution

* Comp. Rend., 52, 538. DINGLER, vol. 160, p. 143.

† Patent, May, 1859.

‡ Examen des Matières color. Saverne, 1861, p. 90.

of shellac produced by boiling 50 grammes of white shellac with 18 grammes of soda crystals in 1 litre of water, is mixed with 50 grammes of a solution of 125 grammes of azaleine (magenta) in $\frac{1}{2}$ litre of alcohol and $\frac{1}{2}$ litre of water. A blue liquid is thus obtained the colour of which is similar to that of a solution of the ammonio-sulphate of copper. By using one litre of water, 100 grammes of soda crystals, and 100 grammes of the azaleine solution, a colour called *Violet de Mulhouse* is obtained.

By treating magenta with the protochloride of tin, M. C. Lauth* obtained an aniline blue. Violet and blue shades may also be got by adding acid salts or free acids to a solution of magenta in alcohol. Instead of alcohol, Mr. E. Kopp† employs methyl alcohol. A blue may also be produced much more easily by adding aldehyd to a solution of magenta in dilute sulphuric acid. In this process the aldehyd is transformed into acetic acid, which, when alcohol is present, combines with it to form acetate of ethyl.

The most important method of transforming aniline red into blue, is the employment of aniline oil for this purpose. This method was discovered by MM. Girard and de Laire; MM. Persoz, de Luynes, and Salvétat described similar processes some time afterwards. The patent granted to MM. Girard and de Laire is dated 24th June, 1862, and its specification is as follows:—

Magenta purified in the usual manner is mixed with its own weight of aniline, and the mixture is heated five or six hours, at a temperature of from 155° to 185° C., keeping it as near as possible to 165°. A violet substance is thereby obtained, which is boiled with a mixture of water and hydrochloric acid until it is entirely purified. For one part of the substance ten or twelve parts of hydrochloric acid, diluted with the same quantity of water, are employed. The acid dissolves the excess of aniline and magenta, which is not transformed into violet, while the violet remains undis-

* Repert. d. Chem. App. Juillet, 1861, p. 3. 273. DINGLER'S Pol. Jour., vol. 162, p. 55.

† Monit. Scient., 1861, p. 338.

solved. It is entirely soluble in alcohol, acetic acid, methyl alcohol, and boiling water containing a little acetic acid. All these solutions may be used at once for dyeing.

To obtain the blue colour, the violet mass is boiled several times with dilute hydrochloric acid (10 parts of the acid to 100 parts of water), and finally washed with boiling water. The boiling is repeated until the colour is pure blue. When cold it has a beautiful copper-like lustre. To use this colour for dyeing, it is dissolved in concentrated acetic acid, alcohol, or methyl alcohol, and the solution thus obtained diluted with water. The liquid resulting from boiling the violet substance with water, contains hydrochlorate of aniline and magenta; it is mixed with an alkali, which precipitates them after a little time.

Instead of producing aniline red, then purifying it and transforming it into violet, the blue colour may be directly obtained by treating aniline with oxidising agents, in which process an excess of aniline must be employed. This method of producing aniline violet and blue has been already mentioned.

According to the specification of MM. Girard and de Laire, it is possible to get every shade of violet, but not a blue. Accordingly, some years after this patent was sold to Messrs. Simpson, Maule, and Nicholson, of London, a manufacturer named Levinstein began to produce aniline blue, and subsequently a law suit was instituted against him by Messrs. Simpson, Maule, and Nicholson.

True aniline blue is always produced from a mixture of aniline red and aniline, by adding an organic acid, an organic salt, or some similar substance to the melted mass. M. P. Bolley* observed that by adding benzoic acid to de Laire's mixture, a good result was obtained. Acetic acid and its salts may be considered the chief agent for the transformation of aniline red into blue; and other organic acids also have the same property. Mr. Price, in his specification,† dated December 10, 1862, says that three parts of aniline

* DINGLER, vol. 168, p. 61.

† Lond. Jour. of Arts, Sept., 1863, p. 146. DINGLER, vol. 170, p. 219.

are to be employed in the form of the acetate, valerianate, lactate, benzoate, tartrate, or oxalate. This is to be mixed with one part of magenta, and heated in a suitable vessel at a temperature of from 150° to 190° C. until the desired shade is obtained. Mr. W. A. Gilbee* mixes at once rosaniline, the base of magenta, with aniline and acetic acid, and obtains aniline blue by heating this mixture. To purify the substance thus obtained, it is poured into exceedingly dilute sulphuric acid. The aniline dissolves, and the liquid is filtered to obtain the blue colouring matter, which is insoluble in water. The blue is then boiled with water until the matter comes away colourless. When cold, the blue forms a resinous mass, which may be dissolved by triturating it with six or eight times its weight of concentrated sulphuric acid. The solution thus obtained is poured into a large quantity of water, which precipitates the colour. By drying the precipitate, the colouring matter is obtained pure. If the solution of blue in concentrated sulphuric acid is heated for twenty-five or thirty minutes before pouring it into water, the precipitated blue is soluble in boiling water, or in water containing a little sulphuric acid.

Mr. Schlumberger's method† differs from the above only by the addition of a quantity of caustic soda or soda crystals to the boiling mass, in order to saturate the acetic acid. Mr. Passavant, of Bradford, uses acetate of soda instead of acetate of aniline, or the mixture of acetic acid and soda employed by the former chemists. He thus gets a colour which he calls a night blue, or *bleu de nuit*, because it appears in full beauty even by artificial light. According to the description of Mr. Passavant's method,‡ 4 parts of magenta are mixed with 8 parts of aniline and 2 parts of acetate of soda, and heated for 2 hours at 200° C. Finally, the temperature of the mixture is raised to 250° C. If the desired shade is obtained, the semi-liquid mass is taken from the fire and poured into 4 parts of alcohol, to which 12 parts of

* Lond. Jour. of Arts, March, 1863, p. 158. DINGLER, vol. 168, p. 141.

† Eng. Patent of Jan. 14th, 1863.

‡ Pol. Centralbl., 1864, p. 971.

hydrochloric acid have been added. The dark brown mass obtained on cooling is ground and then boiled for a quarter of an hour in water containing 8 parts of sulphuric acid. The blue residue obtained by filtration is again heated twice with 8 parts of hydrochloric acid to eliminate the trace of red shade still contained in the blue, after which the mass is boiled several times with water to remove all acid. The dry colouring matter is ground and digested with 10 parts of alcohol until the last trace of red is removed. The method of purification above described is too precise to be carried out in practice, and the temperature need not be raised as described by Mr. Passavant.

For some years acetate of potash has been substituted for the soda salt, because the greenish shade of blue now so popular is obtained more easily by the use of the potash salt. This method was made known in 1864 by Mr. Levinstein, who called the greenish blue *bleu de nuit*; this differs from the *bleu de nuit* of Mr. Passavant, which has neither a reddish nor greenish tinge, but is a pure full blue.

Mr. Levinstein's* description is as follows:—Three parts of aniline are treated with one part of magenta at a temperature of 180° C. until the red is transformed into violet, which is the case after three or four hours. Then half a part of acetate of potash is added, and the temperature is raised to 190° C.; in 1½ hours' time all the red is transformed into blue. The mass is still heated until a small quantity taken out on a white plate appears of a greenish blue colour. Then the mass is treated with concentrated hydrochloric acid, and the *bleu de nuit* is thereby obtained as a solid mass of a red copper-like metallic lustre. The blue which remains dissolved in the acid may be obtained by dilution with water. This colour is generally called *Bleu de Lyons*.

Instead of the acetates Mr. Holliday† of Huddersfield uses benzoic acid, a method long ago introduced into aniline manufacture, and since discontinued. C. G. Williams‡ mixes

* Pol. Centralbl., vol. 65, p. 350.

† Pol. Centralbl., 1864, p. 971.

‡ Ibid., 1864, p. 971.

8 parts of oleate of aniline with one part of rosaniline, or he uses four parts of oxalic acid with four parts of aniline, which mixture he heats to from 180° to 200° C. After a while a dark blue mass, soluble in spirit, is thereby formed. An excess of the acid or of aniline is afterwards eliminated by treating with dilute sulphuric acid and rectified petroleum or photogen, whereby a copper-coloured mass remains, which, when dissolved in spirit, may be used at once for dyeing purposes.

We proceed now to describe the manufacture of aniline violet and blue as it is actually carried on in the aniline manufactories, with the proportions found to be most advantageous in practice.

A reddish violet can be easily obtained by mixing 100 parts of magenta with the same quantity of aniline oil and 25 parts of acetate of soda. The mixture thus prepared is heated in an oil bath at from 170° to 180° C. until the desired shade is produced.

For making violet small distilling vessels are employed of the form already described in the manufacture of magenta. In this case the ingredients are mixed together by agitation. The operation is watched by taking out a little of the liquid and dissolving it in spirit. At first the transformation of red into blue advances slowly, but afterwards more quickly, and at last so rapidly that it is sometimes difficult not to overpass the desired shade. During the whole process a volatilisation of ammoniacal gas occurs, formed, as will be shown hereafter, by the action of aniline on magenta, and at the same time, aniline oil distils over. This is collected and mixed in suitable proportion with another oil, as already described in the chapter on Aniline (page 30); it may then be employed in a second operation.

When the desired shade is produced the vessel will contain a more or less liquid mass, consisting of undecomposed aniline and the red violet colouring matter produced. To eliminate the aniline the mass is ladled out as quickly as possible, and heated with very dilute hydrochloric acid, which dissolves all aniline in the form of hydrochlorate, the violet remaining at the top. This is skimmed off, allowed to cool, and, after powdering, may be sold. Thus prepared,

the red violet colouring matter is a powder much resembling that of magenta, but not so greenish. The bluer the violet the more reddish the shade of the lustre, the pure blue having a decided copper red lustre.

To get the bluer shades of violet the same proportions may be used, but the operation must be continued longer. To manufacture a blue violet, the so-called *dahlia*, the mass is mixed with a small portion of a substance able to transform the reddish blue into a greenish one, as will be subsequently described. The process can thus be completed much more rapidly than in the ordinary way. After taking them from the retorts, the blue violet shades are to be heated with hydrochloric acid, just as the reddish shades.

In the manufacture of aniline blue a mixture of 50 parts of magenta, 150 parts of aniline, and 50 parts of acetate of soda is employed, and the mass is heated as described above. When the colour of the mass has gone beyond the bluest of the violet shades, it becomes a reddish blue. This is a very bright colour, formerly much admired. The substance afterwards turns to a pure blue colour, which has no red or green shade in it; this is the so-called full blue. It was formerly sold under the name of *Bleu de Fayolle*, and can never have been got from a simple mixture of aniline and magenta.

After the blue colour is obtained the mass assumes a greenish blue colour, which is sold under the names of *Bleu de Nuit*, *Bleu de Lumière*, *Bleu de Mexique*, &c. When this shade is also passed the blue becomes of a disagreeable greyish shade, and is now good for nothing. In this case the colour is, as aniline manufacturers say, "overgone."

To obtain easily and quickly the blue shades some additions are necessary, which I shall now describe. When the above-mentioned mixture is transformed to blue violet or a reddish blue the manufacturers add benzoic acid, benzoate of potash or soda, formiate of soda, stearic acid, stearate of soda, common soap, or some similar substance. The addition is made gradually in small quantities, and the mass is well stirred up, and the effect waited for for some minutes. If the effect is still insufficient, a fresh portion is added, and so on till some minutes after the last addition the mass assumes

the desired shade. The mass must then be taken out of the vessel as quickly as possible, for this removal requires a certain time, and even during this time the shade of the colour may be altered ; it is, therefore, best to transform the mass to a shade a little redder than the one desired.

Soap has been largely employed as an addition, especially of late years. By its use blue violet and the several shades of blue are obtained ; the soap used is a common tallow soap, that is to say, impure stearate of soda.

To get a blue violet $\frac{2}{3}$ part of soap is employed where the mixture consists of 1 part of aniline, 3 parts of magenta, and $\frac{3}{4}$ part of acetate of soda. For blue, $\frac{3}{4}$ part of soap is used for every 3 parts of magenta. The liquid mass is taken out of the vessel, as already described in the preparation of violet. Sometimes, if a blue of a certain shade is required, the contents of the vessel are immediately poured into cold water to cool them quickly ; but this action is so uncertain that it is employed only in a few cases. The mass is treated in the usual manner with dilute hydrochloric acid to eliminate an excess of aniline ; it is then washed in pure hot water to purify it from all acid. If stearate of soda or soap has been employed, the stearic acid set free by heating with hydrochloric acid must be removed. This is effected after drying and grinding, by heating the mass with benzol, which dissolves the stearic acid. After evaporating off the benzol the blue colouring matter may be at once used.

The lustre of the blue mass is no longer green but quite red. When the mass is ground to an impalpable powder its colour is blue.

In this operation the weight of the blue obtained always exceeds that of the red employed. In most successful operations 150 parts of blue may be got from 100 parts of magenta.

Both the blue and violet are insoluble in hot and cold water. Only a little undecomposed red can be extracted from the red violet ; but both violet and blue are soluble in spirit, methyl alcohol, aceton, acetic acid, and in glycerin of the specific gravity of 1.2. From all these solutions the colours are precipitated by soluble carbonates, sulphates, acetates, nitrates, and hydrochlorates ; the red shades of violet

are rendered bluer by sulphuric acid and hydrochloric acid. From its alcoholic solution blue is completely precipitated by tannic acid. Heated on platinum foil both violet and blue volatilise ; they are also dissolved by concentrated hydrochloric and sulphuric acid.

By the action of monohydrated sulphuric acid, SO_3, HO , the blue may be transformed into a modification soluble in water. Fuming sulphuric acid is usually employed for this purpose. After the blue has been heated for some time with the acid it is poured into a large quantity of water, whereby it is precipitated as a blue powder soluble in hot water or dilute acids.

The end of the process may be recognised by the circumstance that the blue is then completely soluble in a solution of crystals of soda. The whole of the liquid mass is then poured with constant stirring into a large quantity of cold water, whereby the blue colour is precipitated as a powder which is collected and sold under the name of Soluble Blue. This product is easily soluble in hot water, or water containing a few drops of sulphuric acid. The yield of soluble product is always larger than the common blue employed. A soluble violet has also been obtained in the same way, but the colour assumes a disagreeable greyish shade during the process.

It has been found that the decoctions of certain roots and barks will dissolve aniline colours. Thus M. Gaultier de Chaubry* found that the decoction of the *quillaja saponaria*, as well as the Egyptian soap wort, will do this. The same effect is produced by a decoction of lime soap, and other similar substances.

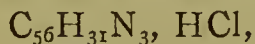
As regards the composition of aniline blue and violet we have already mentioned that all violets may be regarded as intermediate products between red and blue. MM. Girard and De Laire† observed first that when violet or blue was formed by treating the red colour with aniline oil ammonia gas was evolved. Mr. Nicholson afterwards showed that the

* Polyt. Centralbl., 1865, p. 751. Compt. Rend., vol. 60, p. 625. Technol., vol. 26, p. 472. DINGLER, vol. 176, p. 231.

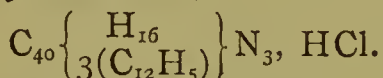
† DINGLER'S Polyt. Journ., vol. 162, p. 279.

blue was a salt of a colourless base. Dr. A. W. Hofmann* then investigated the hydrochlorate of the blue base, which he found to be a scarcely crystallisable substance of a bluish brown colour, insoluble in cold or boiling water and in ether. Alcohol dissolves it and forms a bright blue colour. When the solution is evaporated the colour remains as a film of a lustre half gold and half copper-coloured.

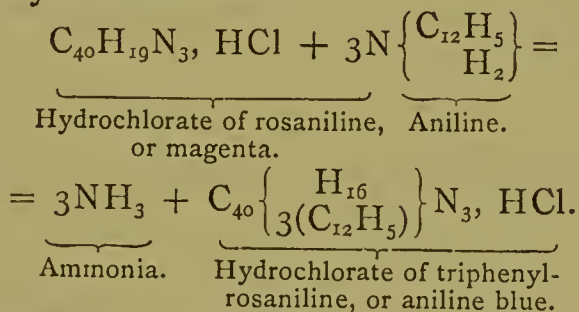
According to several analyses of this substance made by Dr. Hofmann it was found to have the formula—



so that the blue may be considered as the salt of a base differing from rosaniline, $\text{C}_{40}\text{H}_{19}\text{N}$, only by containing three equivalents of the radical phenyl, C_{12}H_5 , instead of three equivalents of hydrogen, and the blue is thus the hydrochlorate of triphenylrosaniline,—



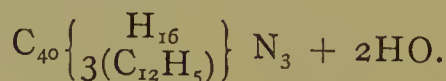
Its formation, during which ammonia gas is developed, may be described by the formula—



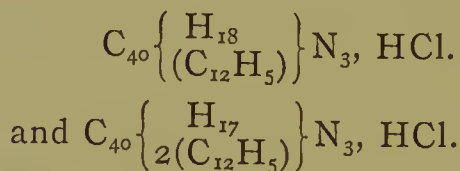
The pure base may be obtained easily by treating the hydrochlorate with alcoholic ammonia, whereupon the whole liquor assumes a yellow colour. It now contains pure triphenylrosaniline and hydrochlorate of ammonia. By boiling the solution thus obtained, ammonia is driven off, and the pure base precipitated of a white or greyish colour. To purify the base dissolve it in alcohol saturated with ammonia, and add a large quantity of water. Pure triphenylrosaniline then rises to the surface as a white coagulum. After washing and drying the precipitate assumes a bluish tint; it melts at 100° without loss of weight. Up to the present

* Compt. Rend., part 59, p. 25. Annal. de Chem. u. Pharm., 1863, p. 437. DINGLER, vol. 170, p. 58.

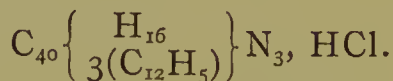
time it has been found impossible to crystallise triphenylrosaniline, although it is soluble in both ether and alcohol. On analysis the pure base is found to be analogous in composition to the hydrochlorate. Its formula is—



As it is impossible to form a true violet by mixing the red and the blue dye together, aniline violet must be an intermediate compound between rosaniline and triphenylrosaniline; either mono- or di-phenylrosaniline. We have explained the composition of the hydrochlorate of rosaniline by the formula $C_{40}H_{19}N_3$, HCl, and the formulæ of the intermediate products must then be taken as—



We may expect the first of these intermediate products to be redder than the second, since the blue hydrochlorate has for its formula—

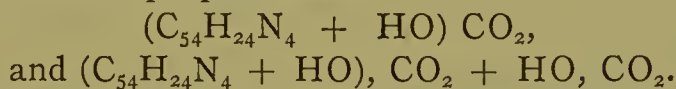


Monophenylrosaniline then produces the red, and diphenylrosaniline the blue shade of violet. It is very probable that the redder shades of violet contain a little of the pure rosaniline, in the same way that the blue ones certainly contain a small quantity of the most substituted product, triphenylrosaniline; and it is found that by treating the reddest shades of violet with dilute hydrochloric acid a little of the red may be extracted.

Mr. W. H. Perkin has separated the basis of his violet (which is obtained by bichromate of potash from the sulphate of aniline) by adding potash to the solution of this purple colouring matter. The solution turns bluish and deposits a black sparkling precipitate. After being dried this substance looks like specular iron ore, and is the basis of Perkin's violet, called by this chemist mauveine. It is so powerful a base that ammonia is expelled by it from its compounds. Mr. Perkin has given to mauveine the

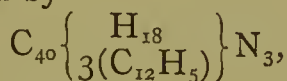
formula $C_{54}H_{24}N_4$, the composition of the hydrochlorate being indicated by the formula $C_{54}H_{24}N_4, HCl$. The hydrochlorate* of this new base is the best known of the compounds which Mr. Perkin has investigated. It is obtained by adding hydrochloric acid to a solution of pure mauveine in alcohol. By boiling the solution prismatic crystals may be obtained of a beautiful greenish metallic lustre. Chloride of platinum produces with the hydrochlorate of mauveine a chloroplatinate of the formula $C_{54}H_{24}N_4, HCl + PtCl_2$, a substance which has a metallic lustre as beautiful as that of the hydrochlorate.

The most interesting compound of this base is its carbonate; no other base derived from aniline forms a salt with this acid. To prepare it carbonic acid gas is passed through a boiling solution of mauveine in alcohol. The liquid is allowed to cool, when it precipitates prisms of the carbonate which Mr. Perkin thinks are a mixture of the mono- and bi-carbonate of the purple base—

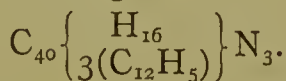


Upon heating, the colour of mauveine and its salts is changed to blue.

Reducing agents decolourise triphenylrosaniline in the same manner as rosaniline. The aniline blue takes up two equivalents of hydrogen, and a substituted leukaniline—triphenylleukaniline—is produced. The composition of this substance is expressed by—



the formula of the blue being—

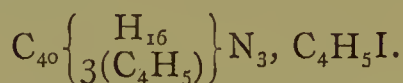


This new colourless base can be produced by treating a solution of triphenylrosaniline, the common blue, with hydrochloric acid and zinc. The solution becomes quickly decolourised, when a large quantity of water is to be added, whereupon a difficultly crystallisable white precipitate is obtained. This precipitate must be separated by washing from the chloride of zinc; it may then be obtained quite

* KOPP, Bulletin de la Société Industrie de Mulhouse, Avril, 1865, p. 167.

pure by dissolving in ether and evaporating. Oxidising agents reproduce triphenylrosaniline from triphenylleukani-line. A little chloride of platinum added to a solution of the latter immediately turns it blue.

We have already shown that it is possible to substitute an organic radical—phenyl, $(C_{12}H_5)$ —for the hydrogen of rosaniline; it is not then surprising to find other radicals replacing this hydrogen. In fact, A. W. Hofmann* has succeeded in substituting for this hydrogen the radicals of the different alcohols—methyl, ethyl, and amyl; the substitution being effected by treating rosaniline in a sealed tube with the iodide of any of the above radicals. The product is an excessively blue coloured mass, giving an alcoholic solution of a splendid bluish violet colour. The dyeing powers of this substance are not inferior to those of rosaniline itself. This product is the iodide of the new substitution base. To obtain the pure substance, take the mass out of the sealed tube, decompose it with caustic soda, and heat the new substitution base, as it is still mixed with a little rosaniline, once more with the alcoholic iodide. By twice repeating this operation a soft resinous substance results, which is transformed by heating with water into a hard crystalline mass of a bright metallic lustre. The pure substance obtained by crystallising from the solution in alcohol yields on analysis the formula—



That is to say, the new substance contains as a basis rosaniline, in which three equivalents of hydrogen are replaced by ethyl (C_4H_5) the radical of alcohol. Even in the hydriodic acid united with this new base the hydrogen is replaced by ethyl, so the new substance must be called ethyliodate of triethylrosaniline.

The salts of triethylrosaniline are known under the name of “Hofmann’s Violet,” and according to the specification of that chemist’s patent of May 22nd, 1863, are made as follows:—

* DINGLER’S Polyt. Journal, vol. 170, p. 62. Comptes Rendus, part 57, p. 25. Journ. f. Chem. und Pharm., 1863, p. 473.

One part of magenta, two parts of iodide of ethyl, and about two parts of strong methyl or ethyl alcohol are heated in a convenient close apparatus at a temperature of 212° F. The vessel used must be made of sufficient strength to resist the pressure of the vapour. The heating is continued from three to four hours, or until the whole mass assumes a violet colour. The vessel is then allowed to cool. When cool it is opened, and the tarry substance dissolved in methylic or ethylic alcohol. This solution may be employed immediately for dyeing.

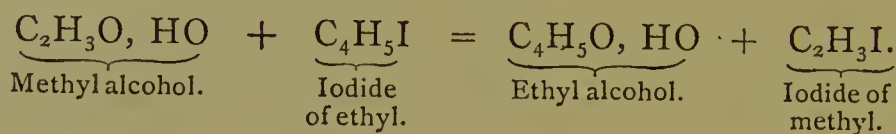
To save the iodine, which is expensive, the above substance when taken out of the vessel may be heated with an alkali. By this process the pure base of this colouring matter is got as an insoluble powder, and the iodine is dissolved by the alkali. The precipitated base must be washed and dissolved in alcohol containing hydrochloric acid. The colouring matter thus produced dyes wool and silk in beautiful red and blue violet shades.

The iodide of methyl, amyl, propyl, or capryl, may be used instead of the iodide of ethyl in the above process, and instead of iodine, bromine may be used. The new violet has a richer colour, and its shades are brighter than those of the common aniline violet. It was at first manufactured by the firm of Simpson, Maule, and Nicholson, to whom the patentee sold his privilege. Soon after, a German manufacturing chemist, Mr. Rudolph Knosp, of Stuttgart, began to make this violet, and it is now made by every continental manufacturing chemist. When dry it has a splendid metallic lustre. It is sold also under the name of *primula*.

In the manufacture of Hofmann's violet on the large scale, the proportion of iodide of ethyl is considerably diminished in order to save the expense of the iodine. According to my own researches, twelve parts of iodide of ethyl are sufficient to transform sixteen parts of magenta into Hofmann's violet.

It is remarkable that German chemists did not at first succeed in producing the blue shades of violet, which are so easily obtained in England, and the bluish shades could only be produced by using iodide of methyl instead of iodide of

ethyl. This interesting point is easily explained, for the methyl substitute formed by using iodide of methyl is of an intensely blue colour. It was not necessary for English chemists to make a direct use of this methyl compound, since at the exorbitant price of alcohol the much cheaper methyl alcohol was always used in England to dissolve the magenta, and to render it capable of transformation. Methyl alcohol yields with iodide of ethyl, at a high pressure, ethyl alcohol and iodide of methyl. The reaction is—



Indeed, after substituting for ethyl alcohol, methyl alcohol, the German manufacturers also obtained bluish violet shades. According to my specification, for 16 parts of magenta and 12 parts of iodide of ethyl, there must be employed 16 parts of methyl alcohol and 2 to 4 parts of acetate of potash, which it is best to dissolve beforehand in the alcohol.

The vessels employed for manufacturing Hofmann's violet consist of iron cylinders coated inside with lead or enamel, and capable of being closed tightly with a lid provided with screws. After filling the apparatus with the above mixture the cover is to be fastened down, and rendered perfectly tight by means of a lead washer. The whole apparatus is then put into a vat filled with boiling water, which is heated by a current of steam. Usually the temperature of 100° C. is exceeded, the apparatus being heated to 110° C., for which purpose common salt or chloride of calcium is added to the water to raise its boiling point. After heating from four to six hours, the red colour is transformed into violet, the shade of which depends on the length of time the heat has been continued. If the same apparatus is always used and it is filled with the same quantity of mixture, the manufacturer learns after a few trials to produce the required shade by regulating the time.

The heating being finished, the apparatus is taken out of the boiling water with a pair of tongs, and allowed to cool,

after which it is opened. The opening must be cautiously effected, as a certain quantity of permanent gas is always produced by the reaction, probably pure ethyl and methyl gas, which being absorbed by the liquid at this high temperature, now suddenly volatilises when the pressure is diminished and may easily cause an overflowing and loss of liquid.

The liquid is then transferred to a distilling apparatus heated by steam, where the excess both of iodide and of alcohol is separated from the solid violet substance. The residue, after distillation, forms a mass of a beautiful metallic lustre, and is a compound of the new ethylated and methylated base with hydriodic acid. To separate it from the latter it is thrown into a boiling solution of soda, which forms iodide of sodium, the pure base floating as a tarry mass of metallic lustre on the top of the liquid. It is to be collected with a ladle, allowed to cool, and pulverised; it is then ready for sale.

By employing iodide of methyl for the ethyl compound, or by adding methyl alcohol to the latter, a methylated base is obtained, the acid compounds of which are soluble in water. A violet thus prepared and afterwards treated with hydrochloric or sulphuric acid, yields soluble Hofmann's violet.

Iodide of ethyl or methyl adapted for the production of violet may be best obtained by a method invented by myself.* According to this method a Woulff's bottle of earthenware is put into a vat filled with straw, into which a current of steam can be introduced through a convenient pipe. One of the openings of the bottle is closed with a tight cork, the other supports a large upright leaden tube, to which it is tightly attached. This tube is closed below by a sieve-like lead plate on to which iodine is introduced from above through the tube. The upper end of the tube is closed in the following manner. Around the mouth runs a gutter lip which is filled with melted paraffin; when the mouth of the tube is covered with the leaden lid which fits into the gutter the tube is perfectly closed. Below the gutter another smaller leaden tube is inserted in the side of the first, and leads up-

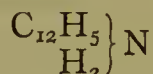
* DINGLER'S polyt. Journ., vol. 181, p. 280.

wards to a coiled worm tube for cooling. Phosphorus in small pieces is put into the Woulff's bottle, and a sufficient quantity of ethylic or methylic alcohol is then added, after which the opening of the bottle is closed by the stopper, and steam is introduced through the pipe into the vat so as to heat the whole apparatus. The alcohol in the bottle begins to boil and volatilises through the vertical leaden tube. When it reaches the worm tube above it is condensed, and runs down again in a liquid state upon the iodine which was placed, as above described, on the leaden sieve-like plate. Here the iodine is dissolved, and passes in the form of an alcoholic solution through the plate into the bottle, where at the high temperature the iodine, alcohol, and phosphorus are transformed into iodide of methyl (or ethyl, according to the nature of the alcohol used,) and phosphoric acid.

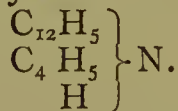
When all the iodine in the tube is consumed, the boiling is interrupted for some moments, and a fresh supply added by taking off the lid of the leaden tube. Large quantities of alcohol and iodine can thus be transformed into iodide without any of the danger which is found to attend the use of all other apparatus. When all the alcohol is converted the liquid is taken from the bottle and washed. Iodide of ethyl being almost insoluble in water is thus obtained pure. The residue of phosphorus in the bottle is heated with fresh quantities of alcohol and iodine until it is quite consumed.

After these remarks upon the acetyl substitutes of rosaniline it now remains to speak of other substitutes* of aniline investigated by A. W. Hofmann.

When rosaniline is heated in a retort a liquid distils which has been found to be aniline. If ethylrosaniline is distilled the liquid obtained is ethylaniline, or since aniline is more properly called phenylamine—

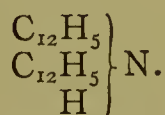


we may call it ethylphenylamine—

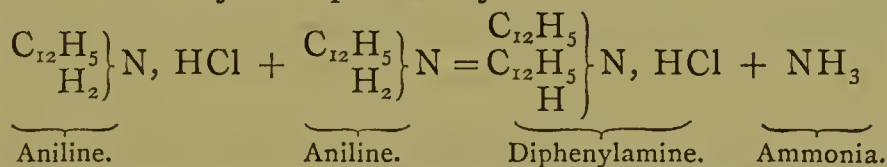


* Jour. Prac. Chemie, vol. 23, p. 208. Pol. Centralbl., 1865, p. 325.

M. Charles Girard, of Lyons, has submitted aniline blue—phenylrosaniline—to distillation, and has thereby obtained at 300° C. a liquid which, allowed to cool, solidified to a solid crystalline mass, the formula of which was found by Hofmann to be—

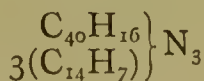


This new substance is therefore a phenylamine (aniline) in which another atom of hydrogen is replaced by phenyl (C_{12}H_5). Accordingly we may call it diphenylamine. Both diphenylamine and its salts yield with oxidising agents blue substances which can be used as dyes. A solution of diphenylamine is instantly coloured blue by nitric acid. MM. Girard and de Laire, of Lyons, have produced diphenylamine in a cheaper manner for manufacturing purposes. They heat in a closed vessel hydrochlorate of aniline with aniline, by which diphenylamine is formed, and ammonia is given off. The reaction may be expressed by the formula—



The diphenylamine thus obtained is transformed into the blue colouring matter by heating in a closed apparatus with bichloride of carbon. M. Briunneyr, of Echternach (Luxemburg), has, however, discovered a new and much cheaper method of transforming diphenylamine into the blue dye.

As aniline yields with rosaniline the aniline blue triphenylrosaniline, so toluidine, the homologue of aniline, gives a blue the compounds of which are similar to those of the common blue, the only difference between the two substances being that the substitution is effected in the case of the aniline blue by phenyl (C_{12}H_5), while in the toluidine dye the radical of this latter, tolyl (C_{14}H_7), takes the place of the substituted hydrogen. Thus, the process of preparation being the same, instead of the phenyl substitute, tritolyrosaniline,—



is obtained. Toluidine blue is more soluble than the common blue, this being almost the only difference between these two interesting colouring matters.

In the same manner in which A. W. Hofmann has obtained a violet colour from rosaniline by means of iodide of ethyl, Mr. W. H. Perkin* has produced a similar colour by treating magenta with the so-called brominated oil of turpentine; his patent is dated Sept. 6, 1864.

To obtain this violet the inventor adds brominated oil of turpentine, manufactured by the process about to be mentioned, to magenta, and heats this mixture with a suitable quantity of alcohol or methyl spirit in a closed vessel at 140° — 150° C., which temperature is continued for eight hours. In this manner, according to Mr. Perkin's specification, a blue violet shade is obtained by filling an enamelled iron vessel with a mixture of one part of magenta and six parts of brominated turpentine. When closed the vessel is heated to 140° — 150° C., which temperature is kept up for eight hours. The vessel is allowed to cool and is then emptied; its contents are dissolved in methyl alcohol, and may be employed at once for dyeing and printing. To get a redder shade of violet three parts of magenta and two parts of brominated turpentine are heated together in the above manner.

Brominated oil of turpentine is obtained by filling a bottle of a capacity of about $2\frac{1}{2}$ litres half full of water. Bromine is then added in sufficient quantity to cover the bottom of the bottle about $1\frac{1}{2}$ inches high. A layer of turpentine oil is poured on the water. On agitation the bromine combines with the oil, which then sinks to the bottom. A fresh layer of oil may be added, and the process repeated as before; thus as much brominated turpentine oil can be obtained as is required. A want of bromine can be easily recognised by the disappearance of the characteristic bromine colour.

* London Journ. of Arts, August, 1865, p. 94. DINGLER'S pol. Jour., vol. 177, p. 405.

CHAPTER VI.

ANILINE GREEN.

It has been known for several years that salts of aniline, especially the nitrate of this base, yield, on being exposed to the influence of the atmosphere, blue and green efflorescences, such as are found on the outside of the vessels containing these salts. But a green dye has only lately been obtained by oxidising aniline salts.

The violet obtained by MM. Depouilly and Lauth is quickly transformed into a green mass by a solution of chlorate of potash. A green precipitate is thus obtained, which at 80° C. assumes a blue colour. The liquid separated, according to Mr. Willm, dyes wool, which after exposure to the atmosphere assumes a green colour.

In 1860 an English patent was granted to Messrs. Lowe, Calvert, and Clift* for producing on the fibre itself an insoluble green colour, emeraldine, which could be transformed by alkalis into blue. The inventors impregnated the fabric to be dyed with an oxidising substance, viz., a solution of 4 ounces of chlorate of potash in 10 pounds of water, dried it and treated it with a solution of an aniline salt containing 1 per cent of aniline. They usually employ for this purpose the tartrate or hydrochlorate of aniline. The fabric is then left to hang for 12 hours in a warm damp place. This method

* Rept. of Pat. Inventions, 1861, p. 199.

is therefore quite similar to that of Mr. Willm. To save one operation the fabric may be immediately impregnated with a mixture of 3 pounds of a solution of the bitartrate of aniline (which contains 1 pound of aniline), 60 pounds of starch, and 1 pound of chlorate of potash. This last is dissolved in the paste while still hot, but the solution of aniline is only added after it has been allowed to cool.

The green colour produced by these methods can be transformed into a blue by washing the fabric with soda or soap. For 10 pounds of water 1 ounce of soda or 4 ounces of soap is used. A solution of 1 ounce of bichromate of potash in 10 pounds of water produces the same effect.

On the same principle is founded the method of producing green. According to the *Muster Zeitung*,* 10 parts of aniline are mixed with 15 parts of nitric acid diluted beforehand with 6 or 8 times its weight of water. The mixture is then thickened by gum Arabic or British gum. To the paste thus obtained are added 10 parts of sugar, and from 4 to 8 parts of pulverised chlorate of potash or soda. Cotton printed with such a paste assumes a beautiful green colour on remaining 24 to 36 hours in the atmosphere. Washed with water containing some acid the samples keep their green colour; treated with an alkaline solution they become blue. This blue can be re-transformed into green by an acid. The green and blue colours therefore are probably different compounds of the same substance, as we have seen so often to be the case.

All the processes above described gave an unsatisfactory result, and therefore a mixture of aniline blue with picric acid was employed instead of a real aniline green. But this had the great defect of not looking well in artificial light, having at night a greyish shade.

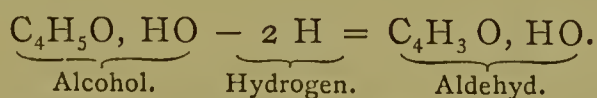
The firm of J. J. Müller and Co., of Basle (now Geigy), succeeded in 1861, after many fruitless attempts, in discovering an aniline green with which dyeing is not more difficult than with any other aniline colour, and whose shades are as bright as possible both in artificial and in sun light. Not long

* 1861, No. 6.

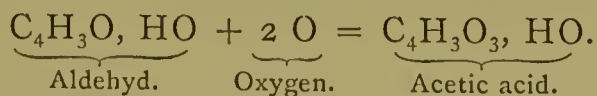
afterwards, also, the firm Meister Lucius and Co., in Höchst, near Frankfort-on-Maine, began to prepare a green colour. Several Rhenish firms then manufactured it also. In February, 1864, a patent was granted to the house of L. J. Levinstein, of Berlin, for a method of preparing a green colouring matter from aniline.

We have already shown that by treating a solution of magenta in dilute sulphuric acid with aldehyd, a violet or blue colour may be obtained. By continuing this treatment the colour is changed into green; but this green is still not durable, and to give it this property another ingredient must be added. Four parts of well crystallised magenta are dissolved in a mixture of 6 parts of common sulphuric acid and 2 parts of water. This solution is heated at 100° C. with 16 parts of aldehyd until the liquid so prepared colours a weak solution of sulphuric acid blue; at the same time the liquid assumes a greenish hue. If the aldehyd employed is impure the colour of the sulphuric acid will be not blue, but reddish blue or a dirty violet. Hence the beauty of aniline green depends in great degree upon the purity of the aldehyd employed. I will here describe the manufacture of this product.

The name aldehyd was introduced by Liebig, the discoverer, and is derived from the words *alcohol dehydrogenatus*. This chemist produced aldehyd by depriving alcohol of a part of its hydrogen:—



It is one of the compounds of the organic radical acetyl (C_4H_3) with oxygen, and contains only one atom of oxygen, the higher oxidised compound of this radical being acetic acid. Hence aldehyd is easily transformed into acetic acid by the addition of oxygen:—



Aldehyd takes oxygen from every substance able to give this element, and is therefore a very strong reducing agent.

In order to obtain a pure aldehyd for the above purpose this substance is produced as follows:—A large retort, provided with a second opening, is filled to the extent of one-third of its capacity with a mixture of 30 parts of bichromate of potash and 32 parts of absolute alcohol. The retort is then put into a sand-bath, and surrounded with dry sand as high as it is filled inside with the mixture. The neck of the retort is fitted to a condensing apparatus, a long metallic worm-pipe being best. Having put a receiver under the opening of the cooling pipe, and a Welter's safety funnel in the tubulus of the retort, we may commence the process.

A hot mixture of 35 parts of sulphuric acid and 30 parts of water are added in small portions to the alcohol in the retort. The liquid within soon begins to boil, and a green scum appears on the top; at the same time a strong current of aldehyd vapour passes over. The cooling must now be very perfect, otherwise the vapours easily cause an explosion. As soon as the reaction of the liquid begins the addition of sulphuric acid must cease; when the first and strongest reaction is over the rest of the sulphuric acid may be poured in. During the whole operation it is unnecessary to heat; heating is even very dangerous, because by the rapid development of aldehyd vapour the whole apparatus may be easily destroyed, while the distillate is weakened by the steam becoming mixed with the aldehyd vapour. Thus produced the aldehyd can be at once employed for manufacturing the green dye. It has an extremely choking odour. As it boils at a low temperature it must be preserved very cautiously.

The solution of rosaniline, treated as before described with aldehyd, is added, with continued agitation, to a boiling solution of subsulphide of soda, by which two different colours are formed. The liquid assumes a beautiful green colour, and a greyish blue substance is suspended in it. The latter is obtained in a much larger quantity than the soluble green, and can only with great difficulty be separated from its solution.

This greyish blue colouring matter can be obtained pure by filtering the solution, and forms when dry a mass of a copper-like metallic reflection. It is sold usually under the

name of *Argentine*. Argentine is obtained in a much larger quantity than the green colour, and the latter being very costly, cannot well be introduced into dye works.

The green colouring matter can be transformed into its bluer shades by saturating its solution with alkalies, and even into blue if supersaturated with carbonate of soda, being at the same time precipitated. The colouring matter thus produced has been sold by some manufacturers, but it can only be dissolved by heating and adding much acid, and its shades are not so bright as those of a green precipitated in another manner.

To obtain a green with a splendid lustre add to its solution a sufficient quantity of acetate of soda, whereby it is precipitated as a beautiful light green mass which may be separated by filtering through cotton. By this process the colouring matter is obtained in a cake, and may be converted into an anhydrous powder by drying at 50°C . The price of this colour was already high, owing to the expensive operations above described, and is heightened still more by this mode of treatment: hence this aniline green can only be employed for dyeing silk, although it is exceedingly beautiful and bright, and appears still more brilliant by artificial light. It is known under the names of Aniline Green, Emeraldine, Viridine, and Aldehyd Green.

According to the specifications of M. E. Lucius'* patent of the year 1864, the production of this green can be effected also by means of hydrosulphuric acid. This chemist dissolves one part of sulphate of rosaniline in a mixture of two parts of sulphuric acid and two to four parts of water, to which he adds four parts of aldehyd, and heats the whole mixture to 50°C . The test whether the solution is sufficiently heated is the same as before. The mixture is then added to from 300 to 500 parts of a saturated solution of hydrosulphuric acid in water, and the whole is heated to 90° or 100°C ., at which temperature 10 or 12 parts of a saturated solution of sulphurous acid are added. After being allowed

* Polyt. Centralbl., 1864, p. 1596 and 1659. Chem. Centralbl., 1864, p. 1095. Polyt. Notizbl., 1864, p. 367.

to cool, the liquid thus obtained is filtered through cloth, in order to separate the greyish blue colouring matter. M. Lucius adds to the green solution from 5 to 20 parts of common salt and a little soda, or carbonate of soda, which effects the complete precipitation of aldehyd green.

It is well known that the product obtained by employing common salt and soda is not of so bright a shade as that produced by the acetate, but now silk dyers usually produce the solution of green themselves, according to the specification of the French chemist Usèbe,* taken out in the year 1863. His process consists in employing 150 grammes of well crystallised sulphate of rosaniline, and 450 grammes of a cold mixture of three parts of sulphuric acid to one part of water. When the red colour is completely dissolved he adds 225 grammes of aldehyd. After again heating and testing in the manner mentioned before, the liquid is added to a boiling solution of 450 grammes of subsulphide of sodium in 30 litres of water. The subsulphide added to the solution, we may remark, seems to be the principal agent of this process; but it is not yet known whether this green is produced by a simple reduction, or by the substitution of sulphur.

A few years ago another aniline green was obtained together with Hofmann's violet. The mixture which produces the violet colour is heated to 110° — 115° C., not as in the production of violet, for four to six hours, but for a much longer time. After opening the apparatus and distilling off the excess of iodide and alcohol there is obtained a mixture of Hofmann's violet and a more or less bluish green colour, which may become even a greenish blue when the operation has been continued for a sufficiently long time. If there is too much violet in the mass, and the green is too blue, it is best to treat the whole once more with the iodide. Some manufacturers treat their product with iodide until the whole or almost the whole is transformed into a green colour, to which they give the yellower shades by adding picric acid.

* 1863, Schweiz. Pol. Zeitsch., 1864, p. 77. DINGLER, vol. 173, p. 76.

French and English manufacturers especially have adopted this plan, because the production of violet in these countries is the patent monopoly of a few firms. In Germany, on the other hand, violet and green are separated by adding a solution of some salt that dissolves the green and leaves the violet colour.

The green solution got by one of these methods can be immediately employed for dyeing, but it is possible to precipitate the colouring matter by adding a solution of tannic acid, usually a decoction of gall-nuts. By drying the precipitate thus obtained, the green colour can be got as a red mass, yielding a green solution in water containing a little acid. It has, however, been found that the green liquid gives a brighter colour to the fibre than the solution of the precipitate, and so the liquid is usually employed as it comes from the manufacturers. It is very interesting that the green colouring matter when dry is red, as the red colouring matter forms green crystals.

CHAPTER VII.

ANILINE BLACK.

No real black can be found among the aniline dyes. In all cases what is called black is really dark green or brown. Real black cannot be obtained in dyeing, and is only represented by amorphous carbon; it cannot be called a colour, but is rather the absence of every colour. Colours produce their impression on our eye by absorbing certain rays of the spectrum, and reflecting others which thus enter our eye. We call black only those substances which absorb all the rays and reflect nothing; from such a substance no ray can be reflected to the eye, and therefore from it we receive no optical impression. A substance really black is thus only seen in contrast with other coloured substances. Such a black, as stated above, is never found in dyeing; the black dyes are only dark blue, green, or brown; and so in this manner may be explained why, although a real black can have no shades, there exists the well known difference between blue black, greenish black, and brown black. If we succeed in obtaining an aniline colour so dark that it gives to the eye the ordinary impression of black, then we may consider that we have succeeded in producing aniline black.

In the chapter on Aniline Green, we showed that a green colour might be obtained by oxidising aniline. Mr. Lightfoot, of Accrington, has obtained in this way a very dark

green, which may be employed as a black. In January, 1863, a French patent was granted him for printing calico with aniline black. This he sold to the firm of J. J. Müller and Co., of Basle, of whom we have before spoken. Mr. Lightfoot employs as agents chlorate of potash, bichloride of copper (CuCl) which by giving up chlorine is transformed into subchloride of copper (Cu_2Cl), hydrochlorate of aniline, acetic acid to liberate chloric acid, and starch paste to thicken the mass. The paste thus made is used for printing, and then the tissue is hung up in oxidising chambers, and washed with a weak alkali. The colour is developed in the oxidising chambers by the mutual reaction of the chlorate of potash and chloride of copper.*

According to M. Käppelin, Lightfoot's paste consists of—

6 litres of water,	
850 grammes of white starch,	
180 ,, chlorate of potash,	
450 ,, hydrochlorate of aniline,	
150 ,, sulphate of copper.	

In this specification the sulphate is employed instead of the chloride of copper. The colour is rendered more beautiful by treating the printed fabric with a solution of bichromate of potash.

On employing the paste it was found that the copper it contained was excessively injurious to certain parts of the printing machines which were made of steel, because copper was precipitated on this metal, and thus the sharpness of the printing rollers was affected. This black paste was also found to weaken the printed fabric, and it was therefore no longer employed, although Mr. Camille Kœchler prevented the effects on steel by preparing the paste without a copper salt, and adding it afterwards by drawing the tissue through a bath of a copper salt. This method was found to be too expensive to be generally adopted.

Soon after, in 1863, another paste was introduced by M. Cordillot, who replaced the copper salt by the red prussiate

* Memoire de M. TH. SCHNEIDER sur le noir d'Aniline. Bull. de la Soc. ind. de Mulhouse, part 35, p. 176. DINGLER'S polyt. Journ., vol. 176, p. 467. Polyt. Centralbl., 1865, p. 1,005.

of ammonia, $3(\text{NH}_4\text{Cy}) + \text{Fe}_2\text{Cy}_3$. This salt is the ammonia compound of the common red prussiate of potash, from which it may be obtained by adding sulphate of ammonia to the solution. By employing this salt M. Cordillot prevented the steel from being affected.

This composition, however, could not be generally employed, because the price of the new paste was very high, and because the temperature at which black was produced could not very readily be secured in the drying chambers of printing establishments. Moreover the black produced by Cordillot's paste was not a fine one, and it also attracted moisture, and separated in large flakes from the tissue. The intensity of this black was much less than that of Lightfoot's product.

M. Käppelin says that Cordillot's paste is prepared as follows:—

A starch paste is made of 27 kilos. of starch, 18 litres of water, 30 litres of gum solution, and 24 kilos. of a solution of gum tragacanth containing 65 grammes of this gum per litre. 24 litres of this paste are mixed with 1,350 grms. of chlorate of potash, and after allowing to cool, 1,900 grms. of red prussiate of ammonia are added. This forms the paste No. 1.

Another mixture, called No. 2, is composed of 26 litres of the above paste, 3,600 grammes of hydrochlorate of aniline, and 3,600 grammes of tartaric acid. The printing paste itself is a mixture of one part of No. 1, and two parts of No. 2.

In 1864, Mr. Lauth took out a patent for a method of printing aniline black on calico, and by this process cotton is still printed with aniline black. Mr. Lauth's paste is the same as that of Mr. Lightfoot, but he adds the copper salt in the form of insoluble sulphide of copper, whereby its action on steel is prevented. After being printed, this compound, being exposed to the influence of the atmosphere, or of the chlorate of potash in the paste, is transformed into a soluble salt, sulphate of copper, and now acts as the oxidising agent. The process is not expensive, and scarcely weakens the tissues at all.

The colour produced is very durable. and can be fixed on the fibre at about 40° C.

Mr. Käppelin has made known* two different pastes made according to Mr. Lauth's principle. In the first paste there is no chlorate of potash, and the sulphide of copper is oxidised by the atmosphere. It is obtained by boiling 800 grammes of starch with 5 litres of water, and adding 270 grammes of sulphide of copper, with a solution of 500 grammes of the aniline salt in 1 litre of water.

The calicoes printed with this paste should pass through the oxidising chamber, and then be drawn through a bath of water to which a small quantity of ammonia or soda has been added. The hot atmosphere of the oxidising chamber simply effects the transformation of the sulphide of copper into the sulphate.

The second printing paste consists, according to M. Käppelin's specification, of 10 litres of starch paste, 200 grammes of chlorate of potash, $2\frac{1}{2}$ kilos. of solution of gum tragacanth, 400 grammes of sulphide of copper, 250 grammes of hydrochlorate of ammonia, and 1 kilo. of some aniline salt, which is added last. The pieces printed with this paste are spread out for 24 hours and drawn through a bath containing two per cent of carbonate of soda, after which they are vapourised and at last washed. The black thus obtained is a full dark colour, and quite insoluble in acids, boiling soap, or alkaline solutions. Acids cause its transformation into green, but every alkali instantly restores the previous colour. A solution of bichromate of potash renders the colour more intense, but a little reddish if employed in too large a quantity. A concentrated solution of bleaching powder causes the colour to disappear, but it is reproduced after a short time by simple exposure to the atmosphere. This patent black has also been bought by the firm of J. J. Müller and Co., of Basle.

On the same principle as that of Mr. Lauth's method, a process of producing black from aniline was patented the 7th June, 1864, by Mr. Edw. Jos. Hughes, of Manchester. In this method 16 ounces of aniline salt are mixed with 4

* Ann. de Génie civil, Avril, 1865, p. 237. Polyt. Centralbl., 1865, p. 1002.

ounces of sulphide of copper and 8 ounces of bichromate of potash, and to this mixture starch paste is added. The inventor employs this method of getting black for dyeing. He then precipitates sulphide of iron or copper on the fibre by any convenient process, and draws the so-treated tissue through a solution of aniline salt and another of chlorate of potash.

Aniline black is very conveniently employed in printing calico, because it can be printed together with most madder and steam colours; but for dyeing its employment is still very limited.

We must lastly speak of a method of obtaining aniline black, which though never employed on a large scale, is yet excessively interesting. This new process* was invented in 1865. It requires no metallic salt, and the oxidation to produce the black is effected by pure chloric acid. From a mixture of hydrochlorate of aniline and chlorate of potash, chloric acid is liberated by the addition of hydro-silico-fluoric acid, which forms an insoluble precipitate with the potash. This chloric acid reacts upon the hydrochlorate of aniline, and effects an oxidation (blackening) of the aniline salt, which is accompanied by evolution of chlorous acid. To develop a beautiful intense black a heat of from 32° to 35° C. is necessary. This new colour can be printed together with every other colour, and as it contains no metallic salt it takes no colour in madder baths.

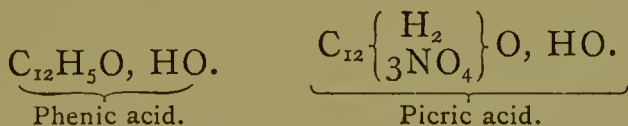
* Bul. de la Soc. ind. de Mulhouse, Août., 1865, p. 345.

CHAPTER VIII.

ANILINE YELLOW.

UNDER the trade name of Aniline Yellow is usually found some form of picric acid or one of its salts.

Picric acid is got by heating carbolic acid (crystallised creosote or phenic acid, $C_{12}H_5O, HO$) with nitric acid, whereupon three atoms of the hydrogen in the phenic acid are replaced by nitric peroxide (NO_4), so that the formula of picric acid differs from that of phenic acid only by containing three atoms of nitric peroxide in the place of three atoms of hydrogen.



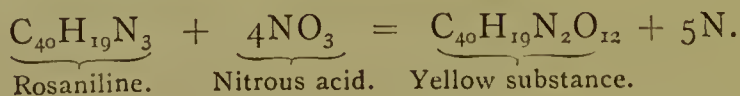
Chemists call the latter compound trinitrophenic acid. With the solution of this substance, wool and silk, and indeed all animal fibres, can be immediately dyed without any previous preparation. Picric acid is always obtained when nitric acid acts upon animal substances, as when leather, silk, or wool are heated with this acid. The action of nitric acid on the skin, whereby it produces yellow stains, is thus explained.

Pure picric acid is a crystallised substance well known to dyers, and often employed by them for dyeing silk and wool yellow and green. It is only sold under the name of Aniline Yellow when its properties are modified by the addition of some foreign materials.

In order to sell picric acid as aniline yellow, manufacturers saturate it with an alkali, and get by evaporating the solution thus obtained a dark yellow amorphous mass. This is offered to the dyers as aniline yellow; it is considerably cheaper than picric acid, and also dyes yellow, but it is not so profitable, as the large quantity of soda or other base employed is useless for dyeing purposes. Its low price and new name caused manufacturers to buy this product without knowing that by it their buildings were exposed to great danger. Though the acid itself burns quietly when ignited, in a similar manner to pitch, the salts are excessively explosive, and have already caused many fatal accidents. Indeed, the picrate of lead is so explosive that it has been proposed for use for filling shells. The compound of picric acid with soda explodes with four times the force of gunpowder, and all the salts of this acid are more or less explosive. Hence dyers must be cautioned against buying such products, and should prove them first by igniting a small quantity, otherwise fatal accidents will probably occur. In Berlin a whole manufactory was destroyed by the explosion of 40 pounds of picrate of soda, and three men were killed.

But there is also a true aniline yellow (*see* page 53) called chrysaniline. To its solutions in water a little acetic acid is added, and then silk and wool may be at once dyed a beautiful golden yellow. It is usually sold under the name Victoria Orange, and is a colouring matter of great intensity and brightness.

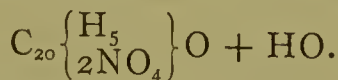
The German chemist Vogel* has discovered that by treating a solution of magenta in water with nitrous acid (NO_3) a yellow colouring matter may be obtained which dyes wool and silk directly of a yellow colour similar to that of picric acid. Vogel has investigated this substance, and his analysis gives the formula, $\text{C}_{40}\text{H}_{19}\text{N}_2\text{O}_{12}$. Nitrogen volatilises during the process, and the transformation is probably—



* Polyt. Centralbl., 1865, p. 1072. Jour. Prac. Chem., vol. 94, p. 453.
DINGLER'S Polyt. Jour.

By passing nitrous acid through a solution of a rosaniline salt in water a brown substance is formed which yields, upon the copious addition of water, a yellow solution. The inventor has called it Zinaline. It is with difficulty dissolved by cold water, but in large quantities by hot. Aniline itself yields, when treated with certain metallic oxides, yellow substances. By treating aniline with antimonie and stannic acid I myself obtained yellow products which dyed wool and silk. An aniline yellow can also be obtained by treating aniline with a solution of antimoniate of potash ($\text{KO}, \text{SbO}_5 + 4\text{HO}$). M. H. Schiff* describes several methods of getting such a yellow. Latterly Mr. Martin has obtained a yellow colour from naphthaline. He took out a patent for this, and sold it to Roberts, Dale, and Co., of Manchester. This yellow is a picric acid in which the organic radical phenyl is replaced by the similar radical naphthyl contained in the naphthaline, a substance got by distilling coal tar, and the white crystals of which we have already spoken of. (*See page 3*).

After having transformed naphthaline into naphthylamine, in the same manner as indicated above in the description of the change of benzol into aniline, Mr. Martin† adds a solution of naphthaline in dilute hydrochloric acid. He then adds a solution of nitrite of potash until a little of the liquid thus obtained gives a cherry-coloured precipitate with alkalis. Nitric acid is then added, and the whole heated slowly to 100° . A large quantity of gas is given off, and small yellow crystals appear at the top, which are collected and purified by solution in alcohol and crystallising out the new yellow colour. It is an acid—the binitronaphthylic of the formula—



This acid and its salts dye silk and wool directly of a reddish yellow colour, but this colour cannot be combined with red colouring matters so as to form a bright scarlet. It is not, therefore, of great importance in dyeing.

* *Annal. d. Chem. u. Phar.* vol. 127, p. 345. *DINGLER'S Polyt. Jour.* vol. 170, p. 157. *Polyt. Centralbl.*, 1863, p. 1664. *Illust. Gewerbe Zeitung*, 1863, p. 386.

† *Monatsbericht der Kgl. Akad. d. Wissen. zu Berlin*, August 8, 1867.

CHAPTER IX.

ANILINE BROWN.

As above shown, the mixture of the substances obtained in the manufacture of magenta by heating aniline with oxidising agents, dyes wool and silk of a reddish brown shade; the higher the temperature employed, the browner is the shade. If the mass is only slightly heated, its solution dyes of a dirty red, but not a brownish shade. This solution looks like a magenta solution, and contains of course all the arsenic acid used for transforming aniline into magenta.

Under the name of Havanna Brown, several manufacturers have long sold the substance we have spoken of, in the form of a powder, which may be very advantageously employed by dyers; only it must be carefully used, as it is exceedingly poisonous. Indeed, this product is often used for getting red-brown shades, and dyes directly the animal fibre of silk or wool. Although it is possible to dye brown with the above product, it cannot be said that it is a true aniline brown, because it is only the mixture of red and dirty violet colouring matters contained in the rough mass that produces brown. By means of water the red can be extracted, and then the dyeing power of this substance is destroyed.

March 17th, 1863, M. George De Laire, of Paris, took out an English patent* for preparing a brown colouring matter

* NEWTON'S London Journal, part 18, p. 349.

from aniline or aniline colours. He melts four parts of anhydrous hydrochlorate of aniline with one part of dry aniline oil. The temperature is slowly brought up to 240°C. , where it must stay until the colour of the mixture, which at first seems not to change, is suddenly transformed into brown. The whole operation lasts for two hours, and may be considered over when yellow vapours begin to make their appearance. The colour thus obtained is soluble in water, alcohol, and acids, and can be used immediately for dyeing. To purify it, it is sufficient to precipitate with common salt. All concentrated saline solutions are able to precipitate the brown colouring matter.

According to a report of Mr. Horace Kœchlin,* to the Mulhausen Industrial Society, a brown can be obtained from leukaniline. Dr. Hofmann has already shown that by treating leukaniline or rosaniline or any of their salts with oxidising agents, brown coloured products are produced, but it was Kœchlin who first sought to fix these colours on the textile fibre. The inventor obtained his leukaniline from L. Durand, who produces it as follows:—A solution of magenta (hydrochlorate of rosaniline) in water is boiled with zinc powder for some minutes after the red magenta colour has disappeared. The leukaniline so produced precipitates in great part from the solution, together with the oxide of zinc which is formed. To purify it the precipitate is treated on a filter with alcohol, by which leukaniline is dissolved. Upon evaporation of the alcohol pure leukaniline is obtained as a yellow resinous substance. To obtain the brown colour from leukaniline, M. Kœchlin uses substantially the method employed for producing black from aniline. The oxidising mixture which he prepares with sulphide of copper is added to the tartrate of leukaniline—



or to magenta. The paste thus obtained is employed for printing like the black paste, and produces when oxidised in the hot chamber a pure dark brown, which resists the action

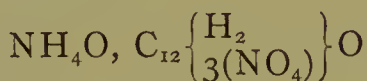
* Bull. de la Société de Mulhouse, Août., 1865, p. 347.

of acids and of alkalies and soap baths. This colour can also be fixed by steam.

This brown may be employed on wool instead of cudbear brown. The printing paste consists of 0.25 litre of a magenta solution, containing 50 grammes of the colouring matter, to 1 litre of alcohol; 0.75 litre of gum mucilage; 50 grammes of oxalic acid, and 25 grammes of chlorate of potash. When mixed as above the paste can be used immediately. With this paste all shades between red-brown and black can be produced; to secure a red-brown, the quantity of chlorate of potash must be diminished, so as to prevent too strong an oxidation. To give a yellow shade to the same colour there must be added a yellow lac, free from protoxide of tin, which by oxidation would produce a reddish brown.

M. Kœchlin obtained a brown precipitate by treating a solution of magenta with chlorate of potash and hydrochloric acid. This precipitate is insoluble in water, soluble in alcohol and sulphuric acid. By means of albumen it can be fixed on cotton.

The picrate of ammonia—



when treated with reducing agents yields a reddish brown substance that dyes wool directly.

At the end of his report on the brown colouring matters obtained from tar, M. Kœchlin speaks of zinc as an agent for decolourising aniline colours when fixed on the textile fibre. The inventor of this employment of zinc is M. Durand, who prints with zinc powder (obtained in the process of distilling zinc), thickened with starch paste or gum, as a corrosive paste, on tissues dyed with aniline red, violet, blue, or green. After steaming and washing, the colour disappears in those places which had been covered by the paste. From magenta, leukaniline is of course formed by means of zinc, and from the blue colouring base triphenylleukaniline, as was before mentioned. Cyanide of potassium produces the same effect.

CHAPTER X.

Determination of the Tinctorial Power and Intensity of the Aniline Colours.

It is of the greatest importance that an aniline manufacturer should know the value of his products in comparison with those of other manufacturers, especially in respect to their power of dyeing animal and vegetable tissues.

Usually to determine the value of a dye it is only necessary to determine how much colour is requisite to dye a certain weight of wool of a certain shade, or how much wool will a certain weight of colour dye to the given shade. The following is the simplest way to answer these questions :—

Five decigrammes of the colouring matter to be tested are weighed out and put into a glass retort, and 50 cubic centimetres of alcohol are added. The liquid is well shaken and heated for a quarter of an hour in a steam bath. The alcohol dissolves the colour, and only a small quantity of carbon which exists in every aniline colouring matter, especially in the blue and violet, still remains undissolved. The solution is allowed to settle, and then poured into a graduated cylinder. The alcohol evaporated during boiling in the retort is replaced by fresh alcohol, with which the retort has been washed out ; there is thus obtained a solution of 1 part of the colouring matter in 100 parts of alcohol (50 grammes of the colouring matter about equalling 50 cubic centimetres of alcohol).

To answer the first question, How much colouring matter is requisite to dye a certain weight of wool a certain shade? proceed as follows:—

In a china basin a sufficient quantity of water is heated until it is too hot to put the finger in. Then one gramme of fleecy wool is weighed, put into the warm water, and moved about with a glass rod until it is thoroughly wetted. It is then taken out, and two cubic centimetres of the colour solution are added and well mixed. The wool is then once more cautiously immersed. It will now be dyed by the solution, and when all the colour is fixed, a fresh portion of the solution is added to the bath, and the operation repeated until the wool is dyed of the desired shade.

The value of the colouring matter under examination is in inverse ratio to the quantity of solution consumed. If five cubic centimetres of the solution of the standard colour were necessary to dye one gramme of fleecy wool a certain shade, and seven cubic centimetres of the colour under examination produced the same effect, the proportion is $7 : 5 :: a : b$, a being the standard colouring matter, and b the colour to be tested. Hence the value of b is $\frac{5}{7}$ ths of that of a .

The answer to the second question, How much wool can be dyed of a certain shade by a certain weight of colour? is not very different from that of the former. A certain quantity of the colouring matter to be tested, equal to that of the standard employed, is put at once into the dyeing pan, and small quantities of wet wool are dyed in the solution to the desired shade. When the colour in the bath is exhausted, the dyed wool is weighed. Then the weight of wool dyed with a given quantity of the tested colour (b) is to the weight of wool dyed by the same quantity of standard colour (a) in direct proportion to the values. If a dyed 1 gramme, and b dyed 1.5 grammes of wool, then the proportion will be $a : b :: 1 : 1.5$, and thus the value of a will be $\frac{2}{3}$ rds of that of b . The former method is usually preferred, as the latter requires more time and pains.

A rough approximation to the value of a colouring matter may be obtained in a short time by the following plan:—Take two bottles of equal dimensions and of about 25 cubic

centimetres capacity, their horizontal section being square, so that there will be the same thickness of liquid in each when the bottles are placed between the eye and a light.

Into one bottle pour a solution of 0.25 grammes of the standard colouring matter dissolved in alcohol, so as to make up 25 cubic centimetres of liquid; call this A. A solution of the colouring matter to be tested is made in the same manner, and poured into the second bottle; call this B. The bottles are then placed side by side and the colour compared. The darker liquid is diluted with alcohol until after agitation the intensity of the colour of the two liquids appears the same. The diluted solution is then poured into a graduated cylinder, and measured; the intensities will be directly as the bulks of the two liquids after dilution.

To distinguish Aniline Colours from one another, and from similar Colours when on the Textile Fibre.

For this purpose M. J. J. Pohl* uses fuming hydrochloric acid and a dilute acid consisting of one part strong acid to three parts of water.

The effects of the fuming acid are observed at the ordinary temperature at the time of application, after 5, and after 15 minutes; also the effect of dilution is then observed. Next the effects of the dilute acid are observed at first and after 15 minutes. Finally, the same test is repeated after a considerable dilution with water.

The following table shows the results of observations made upon the several aniline colours:—

* Pol. Centralbl., 1864, p. 1379. DINGLER, 173, 211.

NAME OF THE COLOUR FIXED ON THE TISSUE.	EFFECT OF THE CONCENTRATED HYDROCHLORIC ACID.		AFTER DILUTING WITH WATER.	EFFECT OF THE HYDROCHLORIC ACID DILUTED WITH A THREEFOLD VOLUME OF WATER.		WHEN DILUTED WITH WATER.
	At once.	After 5 minutes.		At once.	After 15 minutes.	
Aniline Violet	Blue; the liquid turns blue.	Blue; the liquid is blue.	Blue; the liquid is blue.	Violet.	Violet; redder than originally.	Violet.
Dahlia	Dirty brown-red to dark violet; the liquid turns brown-red.	Dirty brown-red, with a greyish shade; the liquid the same.	Greyish green; the liquid is greyish green.	Blue.	Light violet; the liquid dirty red-brown.	Violet; the liquid is blue.
Parme d'Aniline....	As Dahlia.	As Dahlia.	As Dahlia.	As Dahlia.	As Dahlia.	As Dahlia.
Magenta	Violet.	Dark brown; the liquid turns yellow brown.	Dark brown; the liquid is yellow brown.	Violet.	Violet.	Violet.
Coralline; Colour made from Phenic Acid	No variation.	Clearer; the liquid yellow-red.	Colour taken almost entirely from the tissue; the liquid is red.	No variation.	A little clearer; the liquid is light yellow-red.	No variation.
Aniline Blue	Blue.	Dirty bluish green; the liquid light violet.	Dark dirty violet; the liquid light violet.	Blue.	Blue.	Blue.
Bleu de Lyons and Bleu Lumière....	Blue.	Blue; the liquid is colourless.	Blue; the liquid is colourless.	No variation.	No variation.	No variation.
Azurin; Blue colour made from Phenic Acid	No variation.	Blue, with a green shade; the liquid is light blue.	Blue, with a green shade; the liquid is light blue.	No variation.	No variation.	No variation.
Aniline Green.....	No variation.	Light yellow; the liquid is yellow.	Colourless; the liquid is goldish yellow.	No variation.	No variation.	No variation.
Aniline Brown	Almost no variation; the liquid turns brown.	A little clearer; the liquid is dark brown.	Still clearer; the liquid is brown.	No variation.	No variation.	No variation.
Aniline Black	No variation.	No variation; the liquid is yellow.	Dark yellow green to black; the liquid is light olive-brown.	No variation.	No variation.	No variation.

APPENDIX.

REPORT

ON THE

COLOURING MATTERS DERIVED FROM COAL TAR,

SHOWN AT THE FRENCH EXHIBITION, 1867,

*By Dr. A. W. HOFMANN, F.R.S., MM. G. de LAIRE,
and Ch. GIRARD.*

INTRODUCTION.

THIS is no longer an age in which an industry requires many years for its creation, and still longer time for its development and expansion.

Jealously guarding the processes employed, hiding with care the raw materials used, a manufacturing process formerly was hid in an obscurity which had the effect of confining a profitable monopoly to the country where it was first established. The privileges conceded by the rulers, a host of legislative enactments, general ignorance, and the special organisation of labour—all tended, at a period anterior to 1789, to favour this result.

In our days, a useful discovery is scarcely made, or a happy application of one found out, before it is published, described in the scientific journals or other technical periodicals, and especially in the specifications of patents. It then becomes the starting-point of a thousand researches

and new experiments, entered into by the philosopher in the hope of advancing scientific progress, and by the manufacturer with the expectation of reaping a material benefit. From these multiplied and diverse efforts, these incessant labours of an army of workers, arises an industry which has no sooner sprung into existence than it becomes important and prosperous. Moreover, it is not only in the land of its birth where its development takes place; it extends rapidly in foreign countries, so that it not unfrequently happens that the place where the discovery has originated is distanced in the applications of it by neighbouring States. The ocean itself is no longer a barrier between the nations which it separates. New York, in an industrial sense, is now a neighbour of London, Paris, and the German centres of industry.

The history of the artificial colouring matters derived from coal, abounds in illustrations of this. It only dates from the end of 1856, and yet what success it had achieved in the Exhibition of 1862!

From that date, owing to the number, variety, beauty, and value of its products, and from the large scale on which it was carried on, it might rank with the largest industries. In 1862 the value of these manufactures had risen from nothing to 10 millions of francs; at the present day this sum is trebled, and still the products are much cheaper than they were before. Indeed, the improvements successively introduced into the manufacture of the tinctorial products derived from coal, have had the result not only of rendering them more beautiful, but at the same time of reducing their cost in such a manner that aniline colours can successfully compete in price with any other colouring matter of equal tinctorial power; so that if they were formerly purchased on account of the unexampled brilliancy of their tints, they will retain their importance owing to the low price at which they can be produced.

Amongst the colouring matters which were already known in 1862, some have now become true *raw materials*, from which are produced other colouring matters equally beautiful, equally rich, and of no less importance than those from which they have sprung.

Thus, rosaniline has become the parent of a whole series of

colours, and last of all of a green. The gamut of colouring matters derived from aniline is now complete ; we have red, orange, yellow, green, blue, indigo, and violet.

Are we not justified in saying that the manufacture of artificial colouring matters, in spite of the improvements of which it is yet capable, in spite of the discoveries which will yet enrich it, and scarcely ten years old, has emerged from the state of infancy, and become one of the most important industries of the age?

But if the development of this new branch of manufacture has attained so high a point in so limited a time, its publication and diffusion through the industrial and commercial world have advanced with still greater rapidity. The first of the aniline dyes in order of date is mauveine. This was discovered in the month of August, 1856, by Mr. W. H. Perkin. Whilst the inventor, young, and of ample resources, remained for nearly two whole years before he could carry out his invention on a large scale, and strove against the difficulties which beset the introduction of all new discoveries, several French manufacturers produced mauveine immediately, and on a large scale, by the actual process (or but slightly modified) which was revealed to them by the English patent. One who only considered the state of the industry at this time in the two countries, would have said that the invention belonged to France, and had only been imported into England. From France it almost at once spread to Germany.

In 1859, aniline red was produced. Scarcely three months after its production was commenced at Lyons it was transplanted to Mulhouse ; then crossing the Channel, it became established in England, at London, Coventry, and Glasgow, and was not long before it was taken up in Germany.

Aniline blue first appeared in 1860. Less than a year afterwards it took ten manufactories in Germany, England, Italy, and Switzerland to produce this new material.

Whilst the manufacture of aniline colours thus became European, their consumption spread still further : and now could be observed this unique fact in the history of commerce ; the West supplied the East with colouring matters, sending its artificial dyes to the confines of the globe, to China, to

Japan, to America, and the Indies,—to those favoured climes which up to the present time had supplied the manufactories of Europe with tinctorial products. This was a veritable revolution. Chemistry, victorious, dispossessed the sun of a monopoly which it had hitherto always enjoyed: at the beginning of this century, when mythological language was in vogue, it would have been said that Minerva had triumphed over Apollo.

But it was not sufficient to extract colours from tar and send them to China, it was necessary to secure a market for them and get their acceptance; and now occurred a circumstance characteristic of this epoch. In order to apply these colours, the processes being altogether different from those followed by the Chinese, and their employment requiring the assistance of substances which were unknown to them, it was necessary to change at the same time their tinctorial substances, their solvents, and their mordants—in a word, to undertake the education of the Chinese dyers. This difficulty did not for a moment stop the European manufacturer; he sent to China and Japan not only the workmen who should teach his customers the way to apply the colours with which he supplied them, but also the chemical products necessary for their manipulation, such as sulphuric acid and absolute alcohol, which were before unknown to them. Thus arose considerable dealings with the East, the quantities sold by European manufacturers in 1864, 1865, and 1866 amounting to several millions of francs.

The Universal Exhibition of 1867 shows considerable progress in all branches of the manufacture of artificial colours since 1862. It should here be noted that the year of the English Exhibition was itself one of the most fertile in discoveries and improvements.

Almost immediately after its close there appeared aniline green, the violets of methylic and ethylic rosaniline, and aniline black, and at the same time science was able to dispel the darkness which had hitherto enveloped the production of the new colouring matters. If we wished to generalise, we should say that Exhibitions are not only of value in registering acquired discoveries, but still more of inducing and hastening

the birth of new inventions. However this may be, we may here tabulate the colouring matters mentioned in the Reports of the Exhibition of 1862 :—

- Picric acid.
- Isopurpurate of potash.
- Mauveine and its salts.
- Rosaniline and its salts.
- Rosaniline blue.
- Rosaniline violet.
- Chrysaniline (Phosphine).
- Peonine.
- Azuline.
- Emeraldine.
- Viridine.
- Azurine.
- Pseudo-alizarine.

Some of these colours have disappeared from commerce, if, indeed, it is certain they were ever introduced ; these are emeraldine, viridine, azurine, and pseudo-alizarine. The consumption of mauveine has diminished considerably, as well as that of the rosaniline violets ; but, on the other hand, the importance of rosaniline and of triphenylic rosaniline blue has greatly extended. At that time aniline black only existed in theory, now, it is one of the most valuable of this class of colours.

The following is a list of the colouring matters which, since 1862, have entered, or are about to enter, into commerce, and which figured in the Exhibition of 1867 :—

- Aniline green from aldehyd.
- Methylic and ethylic rosaniline violets.
- Aniline green from iodide of methyl.
- Aniline maroon.
- Aniline grey.
- Aniline black.
- Mauvaniline.
- Diphenylamine blue.
- Chrysotoluidine.
- Naphthalic red (salts of chloroxynaphthalic acid).
- Naphthalic yellow (binitro-naphthol).

Amongst these latter substances many are of considerable importance, such as the new greens, the violets, and aniline black.

But if new colours have been discovered, the improvement of the old ones has not been neglected; their price has been lowered; their extreme purity and beauty, which at the date of the 1862 Exhibition were exceptional qualities, have now become matters of ordinary production; and the healthiness of the manufacturing processes have been considerably ameliorated.

Corresponding improvements have been effected in the industry of the raw material. In 1862, a large quantity of coal tar was completely lost for the manufacture of artificial colouring matters; although for some time it was collected in certain works, at St. Etienne, for example, thanks to the care and processes of MM. Pauwels and Knab. The problem consisted in transforming the ordinary coke ovens into vast gas retorts, which whilst producing the same quality of coke admitted of the collection of the tar and gas; the latter serving to heat the ovens themselves. These apparatus, which the limited scope of our report prevents us from describing, are becoming more generally adopted; they have already exercised a notable influence on the price of the products of the distillation of coal, and especially on the light oils, although the tar is far from being collected in a complete manner.

In France three millions of tons of coal are carbonised annually to supply coke for metallurgical purposes. When the process of MM. Pauwels and Knab* is more generally adopted there will be collected from this, 125 or 130 millions of kilogrammes of tar, which would yield 2 or 3 millions of kilogrammes of light hydrocarbons. It may therefore be predicted that the price of benzols will fall still more, and that consequently the cost of colouring matters derived from it will be reduced. These prices are at the present time from 70 to 80 centimes the kilogramme for benzol; in

* *See* La Chimie, by PELOUZE and FREMY, vol. ii., p. 884. The apparatus of MM. Pauwels and Knab also figure in the Exhibition of Mines of the Loire.

1862 it was worth 3 or 4 francs the kilogramme. Aniline, which then cost from 12 to 18 francs, is now worth 2·25 francs, or 3·5 francs at the maximum. Crystallised hydrochlorate of rosaniline has fallen from 250 or 300 francs to 25 and 30 francs. The blue which was formerly sold at 500 francs is now offered at 100 francs, and inferior qualities cost only 30 or 40 francs. These figures prove in a most convincing manner the enormous progress realised by the aniline colour industry since 1862.

This reduction in price of the aniline colours is such that all manufacturers who use colouring matters have found it worth while to replace their former tinctorial products by these artificial colours.

Besides this, the employment of these products has greatly simplified the formerly very complicated and costly operations and processes of dyeing, so much so that an apprentice can now obtain as good shades as a skilled workman; this facility of application has certainly not less contributed to the success of the coal tar colouring matters, than the richness and variety of their shades.

The employment of these magnificent colouring matters is not confined to dyeing and calico printing. They are utilised in many other industries. Their different applications, the most important of which we shall rapidly glance over at the end of this report, have also contributed to their development, although they only consume a comparatively small amount of these colouring matters.

The progress which we are about to record in the industry of the coal tar colours shows, in fact, that the probable development of the aniline colours and their economic and commercial results, foreseen by the Reporter* in 1852, are to-day accomplished facts. Every thing, therefore, leads one to imagine that ultimately the natural will yield entirely to the artificial colouring matters.

This revolution, the influence of which will be most important, since it will liberate for the production of food many lands now employed in industrial operations, would already

* International Exhibition of 1862. Reports of the Juries, Class 2, Section A., p. 120.

have taken place if the artificial colours hitherto discovered were as solid as their rivals. Less fugitive than when first prepared, owing to the greater state of purity in which they are now obtained, they are still too dear to enter largely into the dyeing of cloth and other textures used for household purposes. On reviewing the history of colouring matters in general, we may be permitted to hope that this defect of stability will soon disappear under the combined efforts of science and industry.

Industrial Processes for the Manufacture of Colouring Matters.

We propose to describe successively, and in a succinct manner, the methods which are actually most employed, and are most advantageous for the preparation of the different colouring matters; and we shall especially dwell upon the processes which have been discovered, improved, or made public since 1862. On comparing them with those treated of in the Reports on the London Exhibition, a clear idea will be gained of the changes which time has wrought.

We shall commence by a brief outline of the principal improvements introduced into the manufacture of the raw materials used in the artificial colour industry.

RAW MATERIALS.

1. Benzol, Toluol.

These two hydrocarbons are by far the most important in the industry now treated of. They are extracted from the light oils obtained on the distillation of the tar produced when coal is carbonised in retorts.

The crude tar is submitted to distillation, which is pushed to a greater or less extent according to the uses for which the pitch is intended. Three kinds of pitch are distinguished, only differing from each other in the quantity of heavy oils they contain; the liquid pitch, which contains all the heavy oils; fat pitch, which contains less; and dry pitch, which contains scarcely any.

These different products are employed either as a preservative and disinfectant paint, for the preservation of wood,

for the agglomeration of small coal, or for the manufacture of artificial asphalte.

In the preparation of these varieties of pitch, the light oils which interest us most are always removed. They consist of a mixture of a certain number of liquid hydrocarbons, such as benzol, toluol, xylol, cumol, with a little naphthalin; they contain besides a certain proportion of substances possessing characters intermediate between alcohols and acids, which have been called *phenols*, such as carbolic, cresylic, and xylic acids or alcohols; and there are also present traces of basic substances, such as aniline, picoline, and leucoline.

With the object of purifying the hydrocarbons they are agitated with dilute sulphuric acid, which removes the basic bodies, and then with a ley of caustic soda of sp. gr. 1.34 (40° Beaumé), which dissolves the phenols; the residue is washed several times in water.

The treatment of the mixture obtained in this manner varies in different manufactories, but the isolation of the different bodies is always effected by a series of fractional distillations. Generally the products of distillation are divided into three parts; the first, distilling below 150°; the second, between 150° and 210°; and the third up to 300°. It is principally the first part, known in commerce under the name of commercial benzol, which contains the hydrocarbons used in the manufacture of colouring matters; it boils between 80° and 120°, and contains the whole of the benzol, and the greater part of the toluol.

Mansfield,* to whom we owe the industrial preparation of benzol, was the first who endeavoured to separate the hydrocarbons from crude benzols, and obtained products of a constant boiling point.

The apparatus which he described and employed in 1847, consists of a boiler surmounted by a large condenser of an ovoid form, surrounded by a reservoir full of water. This condenser carries a tube which bifurcates in such a manner as to lead the liquids either into the boiler, or into a refrigerating worm tube.

* J. B. MANSFIELD, patent number 11,960, Nov. 11, 1847. Weekly Evening Meeting of the Royal Institution of Great Britain, Friday, April 27, 1849.

It is obvious, that in proportion as the hydrocarbons in the boiler distil, they heat the water in the reservoir and fall back condensed, until the water has acquired a temperature equal to the boiling point of the hydrocarbons; they then distil over. The boiling point of pure benzol (80°) being below that of water, whilst all the other hydrocarbons contained in the crude benzols boil at higher temperatures, it is evident that during the ebullition of the water in the reservoir, almost all the liquid which distils over consists of benzol. The benzol so obtained freezes easily, and has a boiling point varying within a few degrees only; by submitting it to a second distillation, a still purer product is obtained, and to get it chemically pure it is only necessary then to congeal it and submit the mass to strong pressure.

M. E. Kopp, in 1860,* pointed out the advantage which would be derived from employing, for separating the hydrocarbons, the apparatus used in the rectification of alcohol. In 1863, M. Th. Coupier† took up the same idea, and constructed a distillatory apparatus for the separation of the hydrocarbons. According to M. Coupier, the hydrocarbons, especially the benzol and toluol, occurring in crude benzols can be readily isolated by means of this apparatus.

II. Nitro-benzol.

The production of nitro-benzol and nitro-toluol has made enormous progress since 1862. At the commencement of the aniline industry, this operation offered serious difficulties; but the manufacturer, with habitual perseverance, has surmounted them; he has done away with the dangers of explosion and fire, and has converted a perilous operation, which seemed as if it would never get out of the domain of pure science, into one of the easiest and most elegant of manufacturing processes. Up to 1862 and 1863, nitro-benzol was only made in relatively small quantities at a time. Now the transformation of benzol is effected on hundreds of kilogrammes in one operation.

The operation, which was originally performed in vessels of stone-ware or even glass, is now exclusively effected in

* E. KOPP, *Moniteur Scientifique*, t. ii., liv. 86, p. 829.

† TH. COUPIER'S Patent. Paris, April 4, 1863.

apparatus of iron. The cast-iron vessels which serve for the nitrification, are cylindrical, and of a capacity of 1 or even $1\frac{1}{2}$ cubic metres. They are provided with an agitator moved by steam. The upper portion of the vessel communicates on one side with a chimney to lead away the nitrous vapours, and on the other, by a tube twice curved in the form of the letter S, with a reservoir containing a mixture of nitric and sulphuric acids, the relative proportions of which vary according to the concentration of the acids.

The benzol is introduced all at once into the cylinder, but the mixture of the two acids only comes in drop by drop by the S tube, which, at the same time, serves as a valve.

Experience has shown that it is necessary for the benzol to be attacked as the acid falls into the reservoir, so as to avoid any accumulation of nitric acid at the bottom. This is effected by constantly and regularly agitating the liquid, and by warming or cooling (according to the season) the lower part of the apparatus where the reaction proceeds. With this object the lower portion of the cylinder is surrounded by a serpentine pipe, through which may circulate steam, hot water, or cold water. This arrangement permits of the reaction being hastened or moderated. Finally, the chimney of which we have before spoken, carries on its upper extremity a crown, from which jets of cold water constantly flow and trickle down the sides.

The conclusion of the operation is recognised by the decolorisation of the liquids, which separate into two distinct layers. The acid is removed by means of a stopcock fixed at the lower part of the cylinder, and the crude nitro-benzol is then washed, in the same apparatus, with water containing a little soda in quantity sufficient to saturate the last traces of acid. When the nitrification has proceeded properly, the yield is from 135 to 140 per cent of the benzol employed.

By following the method here briefly described for the manufacture of nitro-benzol, accidents have become relatively very rare; and the workmen are no longer exposed to the nitrous vapours, which some manufacturers condense, whilst others lead them direct to the lead chambers used in the fabrication of sulphuric acid.

III. Aniline.

The transformation of nitro-benzol into aniline takes place under the reducing action of nascent hydrogen. Amongst the numerous methods which have been proposed to effect this reduction, that devised by M. Béchamp is the only one adopted in practice. It consists in submitting nitro-benzol to the action of iron and acetic acid.

The reaction is effected in an apparatus, the first idea of which was due to Mr. Nicholson. With a few modifications it is the one now adopted by most manufacturers. It consists of a large cast-iron tubulated retort (at least 1 metre in diameter and 2 metres high), communicating on one side by its tubulus with a cohobator, and on the other side, by its neck, with a refrigerator; a system of stopcocks allows the products of distillation being turned either one way or the other. The upper part of the retort is besides furnished with a man-hole and an S tube, which can at the same time serve as a safety valve. At the lower part is a hole closed with a screw. In the interior of the retort an axis works, carrying an agitator. The axis is turned by a tube through which steam is brought to the bottom of the apparatus.

In some manufactories the iron and nitro-benzol are charged together, whilst the acetic acid is poured in in small quantities at a time; in others, on the contrary, the nitro-benzol and the acetic acid are introduced together, and the iron is added gradually.

The reduction of the nitro-benzol being very energetic, and giving rise to a considerable disengagement of vapour, the vessel communicates during this operation with the cohobator. To ascertain the end of the reaction it is only necessary to draw off a small quantity of the liquid, which condenses in the worm tube of the cohobator, by means of a tap fixed in its lower part. As soon as the product dissolves completely in hydrochloric acid, the retort is put into communication with the condenser, when the aniline, carried over by a current of superheated steam which is injected at the bottom of the apparatus, is condensed and collected in large

receivers, where it is separated from the water. To avoid the loss of the small portion of aniline which is dissolved in the water, this is used to feed the boiler which furnishes the steam. Thanks to the convenient arrangement of the new apparatus, the transformation of nitro-benzol into aniline, which formerly was a dangerous and an unhealthy operation, is now effected with great readiness, and does not offer the least danger to the workmen. The condensation of the products, which at one time escaped and poisoned the atmosphere of the factory, now materially increases the yield of aniline; and, in fact, by this manner of working there is obtained a result which is generally observed in chemistry, viz., each step made in the direction of healthfulness is an advance in economy.

The perfect condensation effected by the cohobator has also led to a considerable reduction in the quantity of acetic acid formerly employed, and to a consequent diminution in the price of the aniline; and we may add that this new apparatus, which admits of the work being carried out on so large a scale, has also been the cause of many other economies being effected. Finally, the method of distilling by means of superheated steam has greatly augmented the purity of the aniline; it prevents the formation of a considerable number of secondary products, known in factories under the name of *queues d'aniline* (aniline tailings), which are of no value in the production of colouring matters.

IV. Diphenylamine.

Diphenylamine and phenyltolylamine were only discovered in 1864; they were found in the products of the distillation of triphenylic rosaniline and tritolyllic rosaniline.* More recently, at the commencement of 1866, a process has been discovered which permits them, as well as ditolylamine, to be obtained easily, and on the large scale.† This process consists in heating in a closed vessel, under a pressure of six or seven

* HOFMANN, Comptes Rendus de l'Académie des Sciences, 1864, vols. lvi. and lix.

† DE LAIRE and GIRARD's patent. March 21, 1866.

atmospheres, and at a temperature of about 250° , two parts of commercial aniline and one part of hydrochlorate of aniline,

The following is a list of the substances which we are now about to discuss :—

1. Rosaniline and its Derivatives.
2. Substitution Derivatives of Aniline.
3. Derivatives of Phenol.
4. Derivatives of Naphthalin.

ROSANILINE AND ITS DERIVATIVES.

1. Manufacture of Rosaniline and its Salts.

The history of the discovery of rosaniline was given in a detailed manner in the Reports of the Exhibition of 1862, and we will not again recur to it here. Neither shall we occupy more time over the scientific researches undertaken with a view of clearing up the obscurity of its genesis, as these have also been given; but it is impossible for us to avoid pointing out the influence which these researches have had on the rosanilic industry.

Since the commencement of the manufacture of this substance, manufacturers have observed that the success of their operations depended on the nature of the commercial aniline which they had to transform, but without being able to say very clearly what were the causes to which this was to be attributed. They pointed out the existence of a certain relation between the boiling points of the mixture of alkaloids employed, and their yield in colouring matter, but there their science stopped. They confined themselves to distilling, or, to employ the word adopted in these factories, to rectifying their anilines in such a manner that they only employed products distilling nearly between the same limits.

The study of rosaniline, the determination of its composition, and above all, the discovery that this base, far from being a derivative of aniline alone, owed its origin to the

presence of a certain quantity of toluidine in commercial aniline, gave the key to the purely empirical operations of this industry. From this day the rational manufacture of rosaniline commenced; there was no more rule-of-thumb work, and no more uncertainties, for now the manufacturer had something definite to guide him. The boiling points of aniline and toluidine being known, he soon adopted the plan of taking commercial anilines, boiling at different temperatures, and producing artificially the mixture of these two bases in the most appropriate proportions for their transformation into colouring matters. But soon the manufacturer was not satisfied with the ill-defined products met with in commerce. He wished for bodies chemically pure, and the progress of industry soon placed these at his disposal. From that time unremitting attempts were made to prepare the hydrocarbons previously spoken of when treating of the raw materials.

Let us, however, admit that the reaction by which rosaniline is generated, in spite of the assistance furnished by science, still offers some difficulties. According to theory, 30 per cent of aniline and 70 per cent of toluidine ought to be employed; but in practice, although a definite conclusion has not yet been arrived at as to the best proportions to employ, it has nevertheless been ascertained that those pointed out by theory do not give the maximum yield, and that to obtain the best result a larger quantity of aniline must be used. The explanation of that, in our opinion, is that the presence of a certain proportion of aniline, beyond that which enters into the composition of rosaniline, facilitates the transformation by rendering the products of the reaction more fusible. Whatever be the reason, it is certain that the liquid which escapes the reaction and distils over, never has the same composition as the original mixture; it consists of aniline, only containing traces of toluidine.

Leaving the suggestion we have just thrown out for future confirmation, we have to consider the production of rosaniline from an industrial point of view; and we shall enter into some details by reason of its exceptional importance. Indeed, it is not only a colouring matter, economical, very beautiful, and easily applied, but it is the starting-point of a host of

other colouring matters, a true raw material from which we obtain the blue and violets of phenylic rosaniline, the methylic and ethylic violets, the aldehyde green, the iodide of ethyl green, and certain yellow brown colouring matters,—all actually employed more or less.

Of all the numerous agents which at the outset of the aniline colour industry were recommended for the commercial production of rosaniline, arsenic acid* alone has maintained its position, and is now almost exclusively used.

The process which depends upon its employment may be divided into three distinct phases:—

1. The preparation of the crude material, or the transformation of aniline into a salt of rosaniline. 2. The treatment in the wet way of the crude material so obtained. 3. The purification of the salts of rosaniline by crystallisation.

I. Preparation of the Crude Material.

Introduce successively 800 kilos. of commercial aniline and 1,370 kilos. of a solution containing 72 per cent of anhydrous arsenic acid; practically corresponding to two molecules of aniline, one molecule of anhydrous arsenic acid, and five molecules of water.† The retort, of a capacity of about 2,500 litres, is furnished with an agitator moved by steam. A large tube parallel to the axis of the agitator descends to the bottom of the apparatus, and serves to conduct steam into it. At the upper part there is a man-hole, a valve, and a cock which places the apparatus in connection with a reservoir of warm water; at the lower part are two taps for drawing off. The neck of the retort communicates with a large serpentine tube, serving to condense the aniline which volatilises in the course of the reaction. The temperature should not exceed 190° or 200°; the operation lasts 8 or 10 hours; at the end of that time the digestion is terminated. The quantities of water and aniline which distil, serve to control and indicate the progress of the operation; thus the reaction being terminated, there should be collected nearly

* Arsenic acid, which formerly was always prepared by oxidising arsenious acid by means of nitric acid, is now manufactured very economically by passing a current of chlorine into arsenious acid suspended in water.

† A solution of arsenic acid in these proportions does not crystallise even in the winter.

850 litres of a mixture of water and aniline, which, treated by chloride of sodium to effect their separation, will give 440 kilos. of aniline, and 410 kilos. of water. When 800 litres of mixture have passed over, the fire should be withdrawn ; the operation is nearly completed, and the mass is sufficiently warm to admit of the reaction continuing, and the still free aniline distilling over. During this time care must be taken to keep up a continual movement in the still fluid mass by means of the agitator. The quantity of liquid condensed having shown that the reaction is terminated, the drawing off must commence ; the steam-cock is opened, the steam rushes violently into the mass, and mechanically carries off with it the aniline which may still be retained in the apparatus.

When all the aniline has distilled over, gradually introduce boiling water, so as to hydrate the mass. To facilitate this reaction, the retort may be slightly heated again. When a thoroughly homogeneous mass is obtained, which happens in about an hour's time, open the drawing-off taps, and by the aid of pipes transfer the contents to the vats containing the mechanical agitators.

To manufacture, in this manner, 2,000 kilogrammes of crude material per day, four men are employed. When once the operation is set going, only one is wanted until the mass has to be drawn off. The three others are only required at the commencement and end of the operation.

The economy of labour effected by this process is considerable, for by the former methods it required at least ten men to do the same amount of work ; the economy of fuel is equally great ; besides, the operation is healthier, there is no longer any transport of crude material required, and the workmen have not to handle it at the drawing off. This manipulation, so hurtful and deleterious in the old process, is made without the workmen being exposed to the aniline vapours. Moreover, the pulverisation of the arsenical mass, which, in spite of all precautions, caused ulcerations of the nose, lips, and respiratory organs, is entirely suppressed.

Treatment in the Wet Way.—The crude material having reached the vats, is treated with boiling water, in the

proportion of 300 kilos. of crude material, and 1,500 litres of water slightly acidulated with 3 kilos. of hydrochloric acid. At the end of four or five hours the solution is complete. It is run off and strained through large cloth filters, into vast iron reservoirs of a capacity of 8 or 10 cubic metres, where the liquid may be heated by jets of steam. Each reservoir therefore contains about 1,000 kilos. of crude material. The product of the filtration, in which there is no longer anything insoluble in water, contains the aniline red in the state of hydrochlorate, arsenite, and arseniate of rosaniline, besides a large quantity of arsenious and arsenic acids. It now remains to transform the whole of the rosaniline into hydrochlorate of that base, and to separate the excess of arsenic acid contained in the liquid.

To effect this, for every 200 kilos. of crude material contained in the liquid, 204 kilos. of common salt are added, in small quantities at a time. A double decomposition takes place, which is hastened by introduction of steam; on the one hand, hydrochlorate of rosaniline is formed, and on the other, arsenite and arseniate of soda. Hydrochlorate of rosaniline is insoluble in a concentrated saline solution; it therefore separates, and by virtue of its low specific gravity rises to the surface of the liquid. After being allowed to cool, the hydrochlorate is collected, and at the end of four days the mother liquors are run into large reservoirs, where they deposit a further quantity of colouring matter, which they held suspended. The hydrochlorate of rosaniline thus obtained is washed with boiling water in small quantities, so as to remove the common salt with which it is impregnated, and almost all the arsenical salt which it still contains. For some applications it is now fit for immediate use, but it is preferable to let it undergo a crystallisation.

Crystallisation.—The hydrochlorate so obtained is dissolved in boiling water, filtered, and allowed to crystallise. Upon cooling, the liquid deposits crystals on plates which are introduced into the vats. In this manner very beautiful crystals of the hydrochlorate are obtained, and at the bottom of the crystallising vats a crystalline precipitate is found, which may be used for the preparation of the rosaniline blue or violet.

We may remark, in conclusion, that in this process of treatment by the wet way, the workmen are not exposed, as in the old process, to acid vapours sometimes mechanically charged with arsenic or aniline. The reason of this is that before the drawing off, almost the whole of the unchanged aniline is removed mechanically by means of steam, and there is no longer any ebullition of arsenical compounds in the presence of a concentrated hydrochloric acid solution. In the present process liquids nearly neutral are only operated on, and there is therefore a decided advantage from a sanitary point of view.

II. Preparation of Rosaniline.

The process we have just described in detail, gives rosaniline in the state of hydrochlorate. This salt, although sufficiently pure to be employed directly in printing and dyeing, is not sufficiently so for the general demand. A large number of applications demand products of a superior quality, containing no trace of arsenical compounds, and to secure this result the preparation of free rosaniline becomes necessary; besides, the preparation of the derivatives of this substance often requires the employment of the base itself, or at least of some other salt than the hydrochlorate.

Many plans are known for the preparation of rosaniline in the crystalline state; they all depend upon the facility with which salts of this base are decomposed by a solution of an alkali, and on the remarkable property which rosaniline possesses of being only slightly soluble in an excess of alkaline liquids. Practically, solutions of caustic soda, lime, and sometimes even ammonia, are used.

The hydrochlorate of rosaniline dissolved in boiling water is decomposed by an excess of the alkaline solution, also boiling. The quantity of water employed should be sufficient to hold the whole of the rosaniline in solution. The ebullition having continued for several hours, the liquid must be filtered so as to separate a little precipitated rosaniline. Upon cooling, the liquid deposits magnificent, almost colourless, crystals of rosaniline.

This process is simple and easily executed, but unfortunately it requires, owing to the slight solubility of rosaniline, a very large quantity of water.

This difficulty was not long allowed to baffle manufacturers. It was found that by effecting the decomposition of the rosaniline salt under pressure they could not only very considerably diminish the quantity of water employed, but could materially hasten the progress of the operation.

The apparatus by which this transformation is effected is a large closed cauldron of a capacity of one or two cubic metres, heated by steam, enclosed in a jacket, and resembling in all respects the apparatus employed in dye-works for the extraction of colouring matters contained in wood. The solution is effected under a pressure of two or three atmospheres, and lasts four or five hours. If the salt of rosaniline is very pure the whole apparatus is allowed to cool, when by means of a tap placed at the lower part, a magma of crystals may be drawn out and collected on filters. On the contrary, if the salt is not pure, the boiling liquid should be filtered; to effect this the apparatus is furnished with a large tube descending to the bottom and communicating at its other end with a large filtering apparatus, containing a series of filters supported on perforated iron discs. The pressure of the steam in the cauldron determines the ascent of the liquid, which traverses the filters and flows into vats, where the rosaniline crystallises out on cooling.

III. Acetate of Rosaniline.

The general mode of preparing the salts of rosaniline having been already given in the English report of 1862, we will confine ourselves to a special description of the acetate, the crystallisation of which requires the greatest care.

For its transformation into acetate it is necessary that the rosaniline should be as pure and crystalline as possible, but if amorphous rosaniline is employed, it should at all events have been produced from a well crystallised salt. Besides, care must be taken to free it completely from the excess of alkali with which it was precipitated, to dry, well

pulverise, and treat it with acetic acid. This ought to be crystallisable acid, of a perfect purity, and free from sulphurous or sulphuric acids; calcareous waters must not be employed. These precautions being observed, the rosaniline as it comes from the drying chambers is to be introduced into an enamelled iron apparatus, heated by steam or a water bath. The acetic acid is added gradually, and the mixture carefully stirred so as to obtain a homogeneous mass; the brick-red colour of the rosaniline is immediately replaced by the green cantharides reflection, characteristic of the salts of rosaniline. To facilitate the combination the mass is heated for some time to 60° or 70° ; boiling water is then quickly poured over the semi-fluid compound, and the liquid is maintained in ebullition for several minutes. The solution, being run into crystallising vats in a cool place, and at a constant temperature, deposits in two or three days magnificent crystals.

The best proportions are—

Rosaniline	100 kilos.
Crystallisable acetic acid . .	20 „

To dissolve these 120 kilos. of acetate of rosaniline, 240 or 250 kilos. of water are required, which must have previously been brought to ebullition. In this manner crystals of acetate of rosaniline are obtained nearly equal in weight to the rosaniline employed. It is easy to understand that when the acid and the rosaniline are mixed, the temperature should be regulated, as acetic acid distils easily; the same precaution should be observed when dissolving the acetate in water, as a prolonged ebullition drives off a greater part of the acid, and gives rise to subsalts which cannot be made to crystallise.

Acetate of rosaniline may also be prepared by employing impure salts of rosaniline, such as the arseniate or sulphate. Their solution may be decomposed by acetate of lead, producing acetate of rosaniline and arseniate or sulphate of lead. Unfortunately there is also formed a lake with the lead and colouring matter, which greatly diminishes the yield; this process, therefore, is much less advantageous than the former one.

IV. Chrysaniline.

The salts of rosaniline are almost always accompanied by a yellow colouring matter, chrysaniline; it often, indeed, occurs in the crystals, and when very abundant hinders crystallisation. The mixture of these two colouring matters furnishes shades redder than those given by pure rosaniline, which always tend towards violet. It is known in commerce as *yellow fuchsine*.

Two methods exist for separating chrysaniline. That most employed on the Continent consists of crystallising the mixture of the two bodies from acid solutions. The greater part of the salt of rosaniline deposits, whilst the chrysaniline, still contaminated with a little rosaniline, remains dissolved in the mother liquors; these are first neutralised with carbonate of soda, and then precipitated with common salt.

In order to completely purify the chrysaniline, the precipitate is brought into contact with zinc and hydrochloric acid. Under the influence of nascent hydrogen the rosaniline passes to the state of leukaniline, the greater part of which dissolves. It is filtered, and the treatment is repeated several times; the salt of chrysaniline is then dissolved in alcohol, filtered, and precipitated by means of an alkali.

In England, where the treatment of the crude material differs from that we have just described, and where the filtered solution of the crude arsenical mass in boiling water is precipitated at once with lime, the rosaniline separates direct from the alkaline solution in the crystalline state, without any admixture of yellow, the chrysaniline remaining with the lime precipitate.

V. Treatment of the Residues.

The residues resulting from the solution of the crude mass in slightly acidulated water are solid and pulverulent. They consist of a small quantity of rosaniline in the state of hydrochlorate, arsenite, and arseniate, of arsenious acid, of yellow and violet colouring matters, and, lastly, of ulmic products.

A certain quantity of these residues must accumulate before it will be advantageous to work them up. The operation which they have to undergo to extract the rosaniline from

them is altogether similar to that which we have already described in speaking of the treatment of the crude material which furnished them, viz., exhaustion with feebly acid boiling water, decantation, filtration, and lastly, precipitation of the solution with common salt.

A few words more are required respecting the treatment of the residues from which all the salts of rosaniline have been removed, and from which may be separated the other colouring matters which are always formed simultaneously with rosaniline. These substances are three in number, and have received the names of violaniline, mauvaniline, and chrysotoluidine. To separate these three bodies, the residue, after being exhausted as well as possible, is treated with an excess of a dilute and boiling solution of caustic soda, so as to completely remove the arsenical compounds. It is then filtered, and the insoluble mass is washed with boiling water and dried.* To separate the basic colouring matters from the ulmic products, advantage is taken of the solubility of the former in ether, benzol, and especially aniline.

The dried mass is dissolved in aniline and heated to 100° ; a simple filtration separates the ulmic bodies, whilst the solution contains all the colouring matters. Upon saturating the aniline solution with hydrochloric or acetic acid the violaniline is precipitated; the mauvaniline and chrysotoluidine being soluble in an excess of the salt, it is only necessary to filter to separate the violaniline from the two latter substances. Upon diluting with water and adding common salt to the liquid the mauvaniline is precipitated, and a last filtration separates it from the chrysotoluidine, which remains in solution. By saturating the salt of aniline with an alkali, and distilling off the aniline by means of steam, the chrysotoluidine is left behind in the retort.

In this condition the three new colouring matters are not yet completely pure. Their purification may be effected by successive solutions and precipitations.

The salts of mauvaniline are soluble in water, and colour

* G. DE LAIRE and C. GIRARD, French patent, dated February 21, 1867, No. 75,101.

it a magnificent violet mauve colour ; those of chrysotoluidine give a yellow solution ; and those of violaniline, which must be dissolved in alcohol, are blue-black with violet reflections. It is only in the present year that these new colouring matters have been introduced into commerce.

VI. Treatment of the Mother Liquors.—Regeneration of the Arsenic Acid.

The term mother liquors is applied to the liquids which have been used to dissolve the crude arsenical product, and from which the colouring matter has been precipitated either by soda or by common salt. They generally contain large quantities of arsenite and arseniate of soda, of chloride of sodium, and organic salts. It is unnecessary to remark that their composition renders them dangerous, and that consequently they cause some trouble to manufacturers of magenta. From the commencement of this industry, which, in some manufactories, consumes more than 1,000 kilos. of arsenic acid a day, the *Conseils d'hygiène* have devoted attention to obviate the accidents which might be caused by these mother liquors being allowed to flow into water-courses, brooks, or rivers. The only method which, up to the present time, has given, from a hygienic point of view, a radical solution to the problem, consists in evaporating down the mother liquors. The expense of this operation may be met by selling the mixture of arsenical salts to the makers of arsenious or arsenic acids. If this plan is not adopted, there appears no other remedy but reducing the mother liquors to as small a volume as possible, and throwing them into the ocean.

Recently attempts have been made to regenerate directly the arsenic acid contained in these liquids, whether free or combined with soda. To effect this result, it is necessary to evaporate down the mother liquors with a quantity of hydrochloric or sulphuric acid, equivalent to the soda combined with the arsenical acids. By successive evaporations and crystallisations, there are obtained, on the one hand, the soda salts corresponding to the acids employed ; and on the other hand, a solution of arsenic acid. These experiments

have only been carried out on a small scale, and have not yet been adopted in practice.

The difficulties which we have just pointed out as being due to the poisonous properties of arsenic, make it desirable to find another reagent for the conversion of aniline into colouring matters. Indeed, in spite of the advantages which it presents on the score of economy, its inconveniences have prevented it from entirely replacing the agents originally employed. In Germany, for example, some manufacturers, amongst whom we may mention M. Jordan, of Berlin, still use subnitrate of mercury. From all that we have heard, this reagent, employed under proper conditions, will give equally good results with arsenic acid, and by its use are obtained at the end of the operation, not only the mercury in the metallic state, but the nitric acid in the form of nitrate of lime. The product sold by M. Jordan under the name of *rubine* is free from arsenic, and is made in this manner.

COLOURING MATTERS DERIVED FROM ROSANILINE.

I. Blue and Violet Colours obtained by Phenylation.

Aniline blue figured in the Exhibition of 1862, and at that date was largely employed in commerce. The fact that it was derived from rosaniline by the substitution of three equivalents of phenyl or tolyl for three atoms of hydrogen,—a fact which gives its whole scientific history—has been already related in the English jury report of that date. Since then it has been discovered that the violet substances which are obtained at the same time with the triphenyl- or tritolyl-rosaniline, are not simple mixtures of red and blue, but are well-defined bodies, corresponding to intermediate degrees of phenylation or tolylation. We propose to point out the rational processes which permit of the manufacture of these several colours; and as the blue, or triphenyl-rosaniline, is much the most important, we shall commence by describing how it may be obtained.

Blue.—In the preparation of blue, as in that of red, the nature of the commercial aniline, and the proportions of phenylamine and toluidine which it contains, exert a

considerable influence on the product obtained. With a commercial aniline, rich in phenylamine, the blue is principally composed of triphenylrosaniline; but when the toluidine is in excess, it contains more tritolyrosaniline. The triphenylic and tritolylic rosanilines have not exactly the same solubility, they possess different shades, and that of the triphenylic compound is generally preferred. Experience has shown, moreover, that rosaniline is changed into blue more rapidly by phenylamine than by a commercial aniline containing much toluidine; and the product is more easily purified, and requires fewer operations to obtain a good result in the first case than in the second. The aniline employed must therefore be as pure as possible; that which has escaped action in the preparation of the red mass, and has distilled over, will do perfectly for the preparation of the blue when it has been properly rectified.

Theory gives no clue to the kind of salts of rosaniline which should in preference be employed to obtain the blue, but practice has shown that this is not a matter of indifference. In general, salts of organic acids favour the substitution better than those of mineral acids. The acetate, valerianate and benzoate of rosaniline are the most generally employed of all. It is always easy to effect the phenylation on these salts without going to the trouble to make them beforehand; it suffices to add to the mixture of aniline and the rosaniline salt taken, either acetate of soda, valerianate of soda, &c., or acetic, benzoic, or valerianic acids.

In respect to the proportions according to which the aniline should react on the salt of rosaniline, experience has shown that the quantities pointed out by theory should be modified in order to ensure regularity of the operations. In fact, there should be taken three times the weight of aniline which calculation shows is sufficient for the complete phenylation of the rosaniline employed. According to theory, 301 parts (1 molecule) of rosaniline require 279 parts (3 molecules) of aniline, or 100 of rosaniline require 92.6 of aniline to pass to the state of triphenylrosaniline; but in practice from 2 to 3 kilogrammes of aniline are taken for every kilogramme of rosaniline.

This excess of aniline, which at first sight seems enormous, exerts two useful actions : in the first place it admits of the formation of a perfectly fluid solution, and a homogeneous mass during the whole of the reaction ; and in the second place it allows a constant temperature to be maintained in the interior of the apparatus ; and this can approach nearer to the boiling point of aniline, in proportion as the quantity of this substance present is increased.

At the end of the reaction there ought to be left a little more than half the aniline originally present. The manufacturer who omits to collect this will greatly augment the cost of his product. Hence the necessity of working in a distillatory apparatus, or better, in a well arranged cohobator.

These preliminary observations having been made, we shall proceed to the description of the method of manufacturing the blue. It comprises two essentially different operations ; in the first the rosaniline is phenylated, in the second the result of this phenylation is purified.

Phenylation of Rosaniline.—The apparatus employed consists of an enamelled iron retort, holding about 20 litres, heated in a paraffin bath. It is in two pieces, the head and the body, united by pressure screws. The head of the retort should be tolerably high, to facilitate the cohobation of the aniline. Some manufacturers even adapt another cohobator to it, in order to maintain the same excess of aniline until the phenylation of the rosaniline salt is complete. The retort is furnished with a mechanical stirrer, the axis of which revolves in a tube through which steam can pass.

In this apparatus are introduced :—

Acetate of rosaniline . . .	5 kilogrammes.
Aniline	10 „

Heat is then applied, and care is taken, by observing a thermometer inserted in the retort, to keep the temperature stationary at about 190°. The operation lasts about two hours. By successive tests the progress of the operation is watched, and the moment of completion ascertained. A convenient plan is to introduce a glass rod into the retort,

draw it out and make a mark with it on a white porcelain surface ; then add a drop of acetic acid and alcohol. The mark should be perfectly blue, and of a pure colour ; if it is surrounded with a strong red margin the operation is not yet finished. If this border, instead of being of a fresh bright rose colour, has a reddish, brown, or greenish grey tint, the operation has been carried too far to obtain a good blue. These essays permit a skilful operator to see almost exactly how far the reaction has proceeded, and allow him to stop it at the point corresponding to the desired shade. In a well-conducted operation, and with correct proportions, the blue ought to remain dissolved in the excess of aniline, and the reaction terminated, the product should have the appearance of a scarcely fluid, but perfectly homogeneous, mass. The retort is then raised by means of pulleys, and the screws are loosened which fasten the head to the body, so as to allow the contents of the latter to be poured out.

Purification.—The product of the above described operation undergoes different treatment according to the quality of the commercial products which are to be prepared from it. These are very numerous, but they may all be brought under three well-defined categories—direct blues, purified blues, and night blues (*bleus lumières*).

Direct Blue.—To prepare this the treatment of the crude mass is very simple ; all that is required being to separate the blue formed from the excess of aniline. There are two ways to effect this ; the one consists in driving off the aniline by steam, and the other in removing it by methodical washing with dilute acids. The product may then be sent into commerce.

Purified Blue.—There are many methods for preparing this. The crude mass resulting from the phenylation is mixed with alcohol ; it is then poured in a thin stream into water acidulated with hydrochloric acid. Hydrochlorate of aniline is then formed, which remains dissolved in the liquid together with the excess of rosaniline which is not completely phenylated, whilst the blue is precipitated. This is then collected on a filter and washed several times with boiling acidulated water, to remove the brown and reddish substances and the traces of aniline and rosaniline which may still

remain. The success of this plan depends, it will be seen, first on the great state of division to which the blue is brought, and then on the property possessed by aqueous solutions, containing a little alcohol but a large quantity of aniline salts, of dissolving all the foreign matters which accompany it.

Night Blue.—The term night blue (*bleu lumière*) is given to a blue entirely free from violet, and which preserves its clear blue colour in artificial light. It is nothing more than a perfectly pure salt of triphenylrosaniline. To obtain it a good purified blue is taken, such as is given by the preceding process. After several washings with warm alcohol, the residue is reduced to fine powder, dissolved in boiling alcohol, and the solution filtered. To the clear liquid is added ammonia, or, better still, an alcoholic solution of caustic soda; all the blue is precipitated in the state of base. When the ammoniacal or sodic alcohol solution is quite cold, the triphenylrosaniline is collected on a filter, washed once or twice with boiling water, and then treated with the necessary quantity of acid to form a salt. It will be seen that this operation is extremely simple and gives satisfactory results.

Another more complicated process has been employed, and, indeed, is in use at the present time. The purified blue is placed in enamelled retorts with steam jackets, and dissolved in a mixture of alcohol and hydrochloric acid. This liquid is brought to ebullition; part of the alcohol distils off, and it is then allowed to cool, as the hydrochlorate of pure triphenylrosaniline is less soluble than the same salt of other bases which accompany it; it dissolves last and deposits first. The liquid is separated from the blue, which is precipitated. On repeating this treatment several times a tolerably pure blue is obtained. Latterly, endeavours have been made to diminish as much as possible the quantity of alcohol used in the preceding methods by partially or entirely replacing it by aniline; the less volatility of this substance rendering its employment more economical. The mother liquors obtained in all the successive operations of purification should be mixed and carefully preserved. They contain hydrochlorate of

aniline, together with red, violet, maroon, and yellow colouring matters, and when benzoic acid has been employed this is also present in these liquids. They are distilled in an alembic over lime; the alcohol comes over first, then the aniline, which is mechanically carried over by the vapour of water, and there remains in the alembic a residue of benzoate of lime and colouring matters.

Soluble Blue.—Triphenylrosaniline forms with sulphuric acid, as observed by Mr. Nicholson, a true conjugate acid similar to sulphindigotic acid, very soluble even in cold water.

To prepare it take—

Sulphate of triphenylrosaniline	100 kilos.
Common sulphuric acid	400 „

This mixture is heated for about an hour and a half, taking care not to exceed a temperature of 140° or 150° . It is then allowed to cool, and water is added, about eight times the weight of the acid employed. This must be mixed gradually with the sulphuric solution of the blue, with constant agitation. The blue then precipitates in a finely divided state; it is collected on a filter and washed until the liquid begins to run through of a blue colour; this shows that the mass is no longer acid, for the blue sulpho-conjugate acid is insoluble in an acid liquid. It is then dried in a centrifugal drying machine. The dry precipitate is mixed with a slight excess of ammonia in an enamelled iron pan, and heated; the coloured salt rises to the surface as a golden mass; this is collected, broken up, dried, and pulverised, after which it is ready for sale.

II. PHENYLIC VIOLETS.

Phenylic Violets.—Hitherto we have only spoken of triphenylic rosaniline (rosaniline blue); we have but little to add respecting the partially substituted products, mono- and di-phenylrosaniline, and mono- and di-tolylrosaniline. These have not yet been separated or isolated practically, for want of a sufficiently accurate process. The substances which in commerce are known by the name of imperial red violet and

imperial blue violet are mixtures of rosaniline and mono-phenylic, diphenylic, and triphenylic rosaniline, in the first of which the inferior phenylated compounds, and in the second the higher compounds, are present.

Strictly speaking, no very distinct process exists for producing either of these two kinds of violet; it is, therefore, not uncommon for operations commenced with the object of obtaining the red violet, to finish by giving the blue violet. For the preparation of phenylic violets the same apparatus is used as in the manufacture of blue; the mode of operation is in all respects similar to that already indicated for that body, with this difference, that the proportion of aniline employed to phenylate a certain weight of rosaniline is much less when a violet than when a blue is required, besides which the operation lasts a much shorter time.

The discovery of secondary monamines of the phenylic and tolylic series,* and of easy processes for their preparation, suggested the idea of manufacturing rosaniline blue by oxidising a mixture of diphenylamine and phenyltolylamine. The blue colouring matter thus formed is purified by operations analogous to those we have just described. This process is about to be carried out on a large scale.

The progress effected in the manufacture of phenylic blue and violet is shown less by the diminution in price of the products—an important matter certainly, but one dependent on the diminution in price of the raw materials—than by a considerable improvement in the shade of these colours. This is due both to the improved apparatus employed in the manufacture, and also to the discovery of the true nature of the reaction,—a discovery which has enabled manufacturers to devise more rational processes for the production and purification of the rosaniline blues and violets.

Violet Substances obtained by Methylation and Ethylation.—The scientific researches which have established the true constitution of the blue colour, not only had the effect already described of improving the manufacture of the special

* See GIRARD and G. de LAIRE. French patent, 21st March, 1866, No. 70, 876.

colour, but also of leading to the discovery, and then to the industrial preparation, of new colouring matters not less beautiful or important than the preceding. We here see another illustration of the advantages which commerce may derive from the solution of a purely theoretical problem. The scientific analysis of the blue colour, by demonstrating that it was derived from rosaniline by a hitherto unemployed process of substitution (phenylation by means of aniline) immediately suggested the idea of submitting this base to the processes of substitution ordinarily employed in chemistry. The iodides of methyl, ethyl, and generally the iodides and bromides of alcohol radicals, were made to react on this base, and in this manner were formed the methylic, &c., rosanilines, which are known in commerce under the general name of Hofmann's violet.*

The first condition for the investigation of these new reactions was the production on a large scale of iodide of ethyl or methyl, bodies long known as valuable reagents, but not yet employed in manufacturing chemistry. The few difficulties which were at first met with were quickly removed by experience, and now the preparation of these iodides is effected with no trouble or danger. Two kinds of Hofmann's violet are known in commerce—a red and a blue violet. Their modes of preparation are practically the same, the only important difference being in the proportions of the reagents employed.

When operating at the ordinary pressure, the apparatus employed is an alembic heated by means of a steam jacket, and it should be made of copper to prevent the iodide of methyl attacking it. On the one side it communicates with a condensing worm tube, and on the other with an apparatus for cohobation, and by means of properly arranged taps the passage between the alembic and worm tube may be established or interrupted at will. A man-hole admits of the apparatus being charged or cleaned, and a glass tube between the alembic and cohobator enables the condensation, and consequently the progress of the operation, to be watched.

* HOFMANN, English patent, May 24, 1863. French patent, July 11.

1. To make the red violet take—

Rosaniline	10 kilogrammes.
Alcohol	100 litres.
Iodide of ethyl or methyl	10 kilogrammes.
Hydrate of potash or soda	10 „

Heat for about two hours.

2. For the blue violet take—

Rosaniline	10 kilogrammes.
Alcohol	100 litres.
Iodide of methyl	20 kilogrammes.
Hydrate of potash or soda	20 „

These are the proportions which have been found best in practice, but it is evident that there may be many others. These proportions nearly correspond, in the case of number 1, to 2 molecules of iodide of ethyl for 1 of rosaniline, and in number 2, to 4 molecules of iodide of methyl for 1 of rosaniline. With iodide of methyl there are obtained, for equal quantities, a blue product, the solubility of which in water is greater than when iodide of ethyl is used. If the action of iodide of methyl on rosaniline is pushed to the utmost limits, a greenish blue substance is formed, which has been lately employed in dyeing for the production of green shades. We shall speak of this in the section devoted to the green derivatives of rosaniline.

The colouring matter which is produced by this process is a hydriodate of ethyl- or methyl-rosaniline. To purify it distil off the excess of alcoholic iodides and alcohol, and then wash several times with boiling water, so as to remove the iodide of potassium which has been formed, as well as the excess of caustic potash. When the base is completely washed it is dissolved in acid according to the salt which is desired. The salts of ethyl- or methyl-rosaniline are all soluble in alcohol, wood spirit, acetic acid, and mineral acids, and a great many, especially the hydrochlorate and acetate, are soluble in pure water. An excess of common salt, of sulphate of soda, or generally of any neutral salt, precipitates them from their aqueous solutions.

The hydriodates of methyl-rosaniline and ethyl-rosaniline are almost or quite insoluble in either hot or cold water. At

the present time dyers require that the salts furnished to them shall be soluble in water, but at the outset of this industry they had to content themselves with substances soluble in alcohol. Manufacturers of aniline colours found it more profitable to sell the iodine which they left in their product, and which greatly increased its weight, at the price of ethyl-rosaniline. Iodine was worth at that time 24 or 25 francs the kilo., whilst the colouring matter fetched 300 francs the kilo.; this, therefore, explains why, at their first introduction into commerce, the methylic and ethylic violets were generally insoluble in water. Now, on the contrary, care is taken by appropriate alkaline treatment to convert the whole of the iodine into alkaline iodide, from which the iodine is recovered.

In 1865, Mr. Perkin proposed to replace the iodides of methyl or ethyl, in the manufacture of violets, by an alcoholic solution of bromide of terebene.

We should here mention a violet colouring matter which was brought out in August, 1866, and which figured in the Exhibition under the name of Paris violet. This violet, by the way in which it behaved in dyeing, by its reactions, its chemical properties, and its solubility in different liquids, differed in no respect from the ethylic and methylic violets. According to MM. Poirier and Chappat, it is made in the following manner:—In the first instance ethyl or methyl is substituted for the replaceable hydrogen in aniline; the result is ethyl- or methyl-aniline, which is acted upon by one of the numerous agents (bichloride of tin, for instance), which are used to convert aniline into rosaniline, and the result is Paris violet.* The differences which exist between this process and that actually employed in the manufacture of methyl- and ethyl-rosaniline are not such as to preclude the identity of the products prepared by either method.

The process patented by MM. Poirier and Chappat is, as will be observed, double. It includes, in the first place, the preparation of ethylic and methylic derivatives of aniline, and, in the second place, the transformation of these secondary

* POIRIER and CHAPPAT, patent of June 16, 1866.

monamines into violet colouring matters. The method which they have adopted to produce methyl- and ethyl-aniline is that pointed out by M. Berthelot* for producing generally the monamines of the alcohol radicals. This is a new illustration of the introduction of scientific processes into manufactures; and, what is very remarkable, of all the methods which have been employed for the preparation of the methylic and ethylic alkaloids, this, which seems the least practicable in the laboratory, is the only one which is employed commercially.

The publication of these processes gave rise to a reclamation on the part of M. Lauth,† who pointed out that in February, 1861, M. E. Kopp‡ called the attention of chemists to the more and more violet tints of the methyl and ethyl substitution products of aniline red, and that he himself§ had obtained in the July of the same year, a very beautiful violet by the oxidation of methyl-aniline, by means of the reagents employed to transform aniline into magenta.

III. Aniline Green.

There are two kinds of aniline green, one obtained by the action of aldehyd on the sulphuric solution of rosaniline, and another resulting from the action of iodide of methyl on rosaniline. We propose to describe each in chronological order.

Aldehyd Green.—This green was patented in October, 1862, by M. Usèbe. Its discovery some months before is due to a combination of circumstances sufficiently curious to deserve recording, although such occurrences are not unexampled in the history of scientific progress. The following account of this discovery was given to the reporters by the author himself.

A dyer, like all others of his craft at that time, was busily occupied experimenting with the aniline dyes. Amongst

* BERTHELOT, on the production of ethylic and methylic alkaloids by chloride of ammonium. *Ann de Chim. et de Phys.*, 3rd series, vol. xxxviii., p. 63.

† LAUTH, *Moniteur Scientifique*, December, 1866, p. 1082.

‡ E. KOPP, *Comptes Rendus*, vol. lii., p. 363.

§ LAUTH, *Moniteur Scientifique*, July, 1861, p. 336.

other things he tried a reaction which had been described by M. Lauth, at the end of 1861, viz., that of aldehyd on a sulphuric solution of aniline red. In this reaction, a substance is produced which gives to solutions an extremely evanescent blue colour. M. Lauth had given up all idea of utilising this blue colour in practice; and M. Cherpín endeavoured to fix the same colour on silk or wool with similar want of success. His attempts, although fruitless, were incessantly renewed, exhausting his purse, but not his patience. One day, however, discouraged at the want of success attending some recent experiments on which he had founded great hopes, he was on the point of relinquishing the attempt at conquest over this fugitive blue, when the idea struck him to confide his troubles to an old friend, a photographer. A trouble shared is a trouble halved, says the proverb; Cherpín proceeded to test this saying, and experienced the reward of his perseverance and his confidence in the consolations of friendship. He found his photographic friend, and confided to him the history of all his hopes, his experiments, and his fruitless results.—“Fix the blue?” said his friend. “Is that the only difficulty? Why it’s the easiest thing in the world! Have you tried hyposulphite of soda?”—“Hypsulphite of soda? *Mon Dieu*, no! Do you think it will fix my colour?”—“Of course it will. Don’t you know that hyposulphite of soda is the fixing agent *par excellence*, and that when we want to fix anything in photography, that is the substance we always employ?”

Happy he who possesses faith! Cherpín tried hyposulphite of soda, and his joy and admiration of the chemical knowledge of his friend may be imagined when he saw his blue colour metamorphosed into a splendid green, this time perfectly stable. It is scarcely necessary for us to add, that the mode of action of hyposulphite of soda in this case, is entirely different from its photographic action, and that it would be quite impossible to predict the one by knowing the other.

This anecdote contains a moral. It shows, in our opinion, not the result of chance, for that is common to all the world, for where is the discovery to which chance has not more or

less contributed ? but it shows the power of the will, the power of perseverance. Chance only favours two kinds of persons ; those sufficiently instructed, or endowed with talents eminent enough, to observe it, to seize it, and to profit by it ; and those who, by patience, perseverance, and the power of their will, force it in time to become useful to them.

M. Usèbe improved upon the discovery of M. Cherpin, and rendered it industrially available. The green produced by this process is very beautiful, and has been rapidly adopted in commerce for dyeing and printing ; but in spite of the efforts of M. Usèbe, and especially of M. Müller, of Bâle, it has not yet become the basis, of a large chemical manufacture, like aniline blue or red.

The explanation of this is, that after the colour has been prepared for a certain time, it loses its freshness, and ultimately becomes destroyed. Most dyers, therefore, prepare the green for themselves, and only make it in proportion to their immediate requirements.

Each dyer has a formula which he thinks gives the best results. The following proportions are much employed :—

Aniline red	300 grammes.
Mixture of 3 parts of sulphuric acid	
and 1 of water	900 „
Aldehyd	450 „

The aldehyd should be added gradually to the cold solution of sulphate of rosaniline, and when it is all mixed, the whole is heated on a water bath until the mass is completely homogeneous. From time to time a drop of the mixture is taken out on a glass rod, and thrown into slightly acidulated water. When a fine blue solution is obtained the reaction is arrested. The whole is then poured into 60 litres of boiling water, containing in solution 900 grammes of crystallised hyposulphite of soda ; the mixture is boiled for a few minutes with a current of steam, and filtered. All the green remains in solution, whilst a kind of greyish blue colouring matter is collected on the filter. This green liquid, prepared as above described, constitutes an excellent dye-bath for silk or wool, provided it is used at once.

Some makers of aniline green employ slightly different

proportions. They dissolve 1 kilo. of pure crystallised sulphate of rosaniline, in 2 kilos. of sulphuric acid of sp. gr. 1.63, at 66° B., mixed with 500 grammes of water. When the solution is homogeneous they add 4 litres of a concentrated alcoholic solution of aldehyd. At the end of half an hour the reaction is nearly terminated; the mixture is then poured into 100 litres of water, containing 4 kilos. of crystallised hyposulphite of soda, the whole is boiled for ten minutes and filtered, to separate the greyish blue from the green which passes through with the liquid. To precipitate the green, acetate of soda and tannin may be employed; a precipitate is thus produced, which may be dried, but it is more commonly sold in the form of paste: this is only used in printing.

The greatest uncertainty still exists as to the chemical constitution of aniline green. We are, however, justified in hoping that this will soon cease to be the case; aniline green is now a commercial substance, manufactured on a large scale, and is becoming more and more pure every day. After having presented to science a problem, without furnishing the data necessary for its resolution, manufacturing industry is working to fill up the gap, and everything leads us to anticipate a successful result.*

Iodide of Ethyl Green.—When methylic and ethylic violets are treated with boiling water, a greenish blue substance remains in solution; the liquid is mixed with carbonate of soda, which precipitates a little violet, whilst the green remains dissolved. To extract this, a concentrated solution of picric acid is added to the solution, when a green colouring matter is precipitated; this is collected on a filter, and washed two or three times with cold water. Manufacturers of artificial colours have only commenced to introduce this new green substance commercially, since the year 1866. It is generally sold in powder, and is preferred in dyeing to the green prepared with aldehyd. Nothing is yet known as to its chemical composition.

* Dr. QUESNEVILLE informs us that since the publication of this report MM. Girard and de Laire have obtained aniline green in the crystallised state, giving the most brilliant results in dyeing.

SUBSTITUTION DERIVATIVES OF ANILINE.

I. Mauveine and its Derivatives.

The history of the discovery of mauveine, and the different processes for its manufacture, have already been given in the Reports of the Exhibition of 1862. All that now remains to record is, that since that date, its composition has been determined.

Blue.—Attempts have been made to prepare substitution products from mauveine. Upon submitting it to the action of aniline, under the same conditions employed to obtain triphenylic rosaniline, a blue colour is produced, but one whose tint is neither so rich nor agreeable, and which has not been adopted in commerce.

Grey.—Upon treating with aldehyd a sulphuric solution of mauveine, a colouring matter is produced, which dyes fabrics a flaxen grey. The mode of applying this substance is very easy; but unfortunately, its price is still very high, on account of the value of mauveine, which is still 100 francs the kilo. This would prevent the derivatives of the mauveine series from acquiring an importance at all comparable to that of the rosaniline series, even if their shades were equally perfect, which they are not.

The constitution and the composition of aniline grey are as yet unknown, as it has not yet been the object of any scientific study. M. J. CastelHaz has taken out a patent for the following preparation:—Dissolve 10 kilos. of mauveine in paste, in 11 kilos. of sulphuric acid, at 66° B. After having added to the mixture 6 kilos of aldehyd, allow it to stand four or five hours. Then throw the mass on a filter; the grey passes through, and may be precipitated by a salt. It is purified by solution and precipitation repeated two or three times.

II. Aniline Maroon and Brown.

Many brown and maroon colouring matters exist which are made from commercial aniline, but their mode of preparation is still obscure. The first was pointed out by Mr. Perkin in 1863, as a secondary product of the reaction

which produces mauveine ; a second results from the action of an oxidising agent on ditolylamine ;* and a third is obtained by the action of hydrochlorate of aniline on a salt of rosaniline. This last having proved of most commercial importance, we will give the mode of its preparation.†

A mixture of 4 parts by weight of hydrochlorate of aniline, and 1 part of a salt of rosaniline and a mineral acid (the hydrochlorate, sulphate, or phosphate, gives the best results), is heated to 240°, and the mass maintained in ebullition until the colour, which is at first of a beautiful red violet, and apparently undergoing no change, suddenly passes to maroon. The operation lasts for one or two hours, and its approaching termination is known by the appearance of yellow vapours, which condense in the cold parts of the apparatus. The maroon substance thus obtained is soluble in alcohol, ether, benzol, and acetic acid, and it is precipitated from its solutions by alkalies and neutral salts in concentrated solution. These properties enable it to be purified ; it can then be employed in dyeing, and gives very beautiful shades on silk and leather.

III. Aniline Black.

Up to the present time, aniline black is not a definite chemical compound, a substance which can be produced in the isolated state ; it is not even a product which has assumed a commercial form. It is necessary to be produced direct on the fabric, and, if we except some quite recent endeavours to apply it to dyeing, it has hitherto been used only in printing. Aniline black therefore scarcely enters into our province, since it is not the object of a chemical industry properly so-called ; nevertheless, its importance in the calico printing trade, and its probable, almost certain, application to dyeing, will not allow us to pass it over in silence.

Aniline black was introduced into commerce towards the end of 1862, and patented in France, in January, 1863, by Mr. John Lightfoot, of Accrington. It may be said to have

* GIRARD and DE LAIRE, *Comptes Rendus*, vol. lxxiii., p. 964.

† GIRARD and DE LAIRE, Patent of March 23, 1863.

actually existed since the year 1860 ; it was indeed produced by the process described by Messrs. Crace Calvert, Charles Lowe, and Samuel Clift, for obtaining dark blue and green colouring matters.

The process patented by Mr. Lightfoot has this peculiarity, that the black colour does not exist at the moment the tissue is printed on, but is gradually developed on the fibre as the result of reactions which are set up between the bodies constituting the mixture, in contact with atmospheric oxygen at a certain temperature. It consists of printing on the fabric with a mixture of—

Chlorate of potash	25 grammes.
Aniline	50 „
Hydrochloric acid	50 „
Bichloride of copper (of 1·44°)	50 „
Sal ammoniac	25 „
Acetic acid	12 „
Starch paste	1 litre.

The fabric, after having been printed on and dried, is exposed to the air in oxidising chambers for about two days. After this time it is washed in feebly alkaline water, and the black which has become developed in the oxidation chamber will be fixed. The acid of the aniline salt determines the decomposition of the chlorate of potash, and at the same time the bichloride of copper reacts on the aniline. The result of this reaction is the production of aniline black, which is quite insoluble, and remains fixed on the tissue.

The new colour was at first received favourably, and was immediately adopted in Switzerland, Germany, England, and France, but it was soon almost entirely given up, owing to grave faults which attended its practical employment when prepared in this manner. The large quantity of bichloride of copper which it contains causes it to corrode the steel or iron cylinders used in calico printing, and impairs the strength of the fibre. Moreover, its great acidity prevents it being kept long at the ordinary temperature without decomposing. The reaction then takes place before the printing operation, and the black cannot be fixed.

Many manufacturers and chemists have tried to modify the formula of the inventor, and overcome the difficulties of its employment. Each printer added something to the mixture prescribed by Mr. Lightfoot, working by a process which was perfect in his own eyes, and which he took great care to keep as secret as possible. It was not until January, 1865, that M. Lauth succeeded in remedying the principal inconveniencies which attended the production of aniline black produced by Mr. Lightfoot's process, by simply substituting sulphide for bi-chloride of copper. This sulphide is changed into sulphate by the oxidising action of the chloric acid, the chlorine, or one of the chloro-derivatives produced by the action of chlorate of potash on hydrochlorate of aniline. The conditions then become similar to those in Lightfoot's process, with this difference, that the soluble salt of copper does not exist in the mixture before it is impressed on the fabric. It is then formed gradually and simultaneously with the aniline black, and is decomposed at the same time, consequently, there is no corrosion of the machinery or cylinders, and no particular deterioration in the strength of the fibre. To these advantages must be added the fact that the colour prepared with sulphide of copper will last a long time, and that it is of an easy oxidation. Thanks to this improvement, aniline black is now used on a large scale, and although its employment demands a certain amount of skill so as to avoid injuring the fabric, it has come into general use.

The following are the proportions ordinarily employed; heat and digest together:—

Water	500 grammes.
Starch	1000 „
Sulphide of copper	250 „

Afterwards prepare the following mixture by the aid of heat:—

Water	1850 grammes.
Torrified starch	1200 „
Solution of gum tragacanth		1 litre.
Hydrochlorate of aniline	800 grammes.
Chloride of ammonium	100 „
Chlorate of potash	300 „

These are allowed to cool and then mixed together ; they are applied in the usual manner. The black is developed in the oxidation chambers at a temperature of between 20° and 30°, under the double influence of the oxidising agents employed, and the atmospheric oxygen. At the end of 24 hours the fabric is washed.

The nature of the aniline salt which forms part of the mixture is a matter of some importance ; neither the acetate nor the citrate of aniline can be employed to give the black, and hitherto printers have only employed successfully the hydrochlorate or the nitrate. The more acid the aniline salt is, the more intense is the black, and the more rapid its development. Unfortunately the ill effects of too great acidity of the colouring material, in respect to deterioration of fibre, and corrosion of the metallic apparatus employed, render it necessary to use the aniline salts as neutral as possible.

By varying the process which gives aniline black, other shades which approach it, more or less, have already been obtained. Thus, with the following receipt, M. Sacc has obtained brown and olive tones of great body—

Water	300 grammes.
Flour	36 „
Chlorate of potash	15	„
Acetate of copper	15	„
Nitric acid	10 „
Aniline	20 „

Aniline black may be employed as a more solid basis for composite colours than logwood or iron, and thus admits of the production of a vast number of shades. It perfectly supports dyeing with garancine, and all the operations employed to produce red and garancine rose colours. It is unalterable in the strongest acid or alkaline baths ; it resists most oxidising agents, and all temperatures employed in steam and oxidation chambers, and it may therefore be associated with all metallic steamed colours. The action of steam, however, gives the black a slight green tinge.

In short, it may be said that aniline black is very superior to all the other blacks employed in dyeing, and it would be an immense boon to industry if means were discovered to

render it applicable to printing on cloth; hitherto it has shown but slight affinity for wool. On the other hand, it fixes itself perfectly without mordants on vegetable fibres.

No solvent is known which is capable of removing aniline black when once fixed on a fabric; it may be said to be completely indelible.

In the month of August, 1865, M. Paraf proposed a mixture of hydrochlorate of aniline, chlorate of potash, and hydrofluosilicic acid as giving a very beautiful black, and not weakening the tissues. Some time after M. Rosenstiehl pointed out that a mixture of chlorate of ammonia and hydrochlorate of aniline would give a very fine black. These receipts indeed produce a very good colour, but on condition of their being applied with a copper or bronze cylinder; when the above-named mixtures are printed with a plate or cylinder of wood, so arranged as to absolutely avoid the presence of copper, nothing is obtained beyond a dirty blue. But if to this mixture, which only gives a blueish grey, increasing quantities of copper are added, from 1 milligramme up to 1.5 grammes, the grey darkens more and more, until finally a very fine black is obtained. It appears from this experiment, which is due to MM. Lauth and Rosenstiehl, that copper is an essential element of aniline black.

M. C. Kœchlin, who has worked a great deal on aniline black, is not of this opinion. He believes that copper is not one of the necessary constituents of aniline black. He thinks that the copper which is always obtained by the incineration of a tissue printed with aniline black is there present simply in the state of mixture, and that it can be completely removed, without altering the black colour, by thoroughly washing the fabric in acid liquids.

According to this chemist a black is prepared, identical with that produced on fabrics, by boiling together the following mixture :—

Aniline	100 grammes.
Hydrochloric acid . . .	100 „
Ferrocyanide of potassium	50 „
Chlorate of potash . . .	50 „
Water	4000 „

After three or four days' maceration (the author does not say whether hot or cold), it must be filtered to collect the residue, washed in water, exhausted by alcohol, then treated with an acid, and finally by slightly ammoniacal water.

It has never been demonstrated that the substance so obtained is quite identical with the black produced on tissues by the aid of a copper salt, neither has it been shown that aniline black is a single compound. On the contrary, according to M. E. Kopp, it is a mixture of several colouring matters, of emeraldine, azurine, and all the colours which are produced upon oxidising a mixture of aniline and toluidine. But this opinion is not very probable, and the objection may be raised against it that it is unlikely for a mixture, as in this case, to possess none of the chemical properties of its constituents. The solvents of the red, violet, blue, green, and yellow dyes do not dissolve the black, and its affinities for vegetable or animal fibres is the reverse of those possessed by the colours just enumerated.

To sum up, the chemical history of this black is yet to be ascertained, and all that is known of it is a few of its properties. It is completely insoluble in hot water, alcohol, ether, benzol, boiling soap, alkalies, and acids; it is slightly soluble in salts of aniline; it is of a very rich velvety black; acids change it to green, but alkalies bring it back to its original shade. Dilute bichromate of potash increases its intensity, but when concentrated, reddens it. Chlorine and alkaline hypochlorites destroy its colour after some time; but, according to M. C. Kœchlin, when the action of chloride of lime on aniline black has not been sufficiently prolonged for its tint to be completely destroyed, but only to have been brought to a garnet red, a very curious phenomenon is observed. The original black colour gradually reappears, until finally it becomes of the same intensity which it was before the action of the chloride of lime.

DERIVATIVES OF PHENOL.

I. Phenic or Carbolic Acid.

Carbolic acid, discovered by Runge* more than 40 years ago in oil of coal tar, and since specially examined by Laurent,† has only been prepared commercially since 1840, when the latter chemist published the results of his important research. Indeed almost the whole of the creosote at this time met with in commerce was more or less pure carbolic acid, and was produced almost entirely in Germany, principally at the chemical works of M. E. Sell, of Offenbach. It is however, to Dr. Crace Calvert, of Manchester, to whom belongs the merit of having first prepared this body in the crystalline form, and of having in this manner greatly contributed to facilitate and extend the numerous applications of which carbolic acid is susceptible.

The improvements effected in the manufacture of aniline dyes could not fail to influence the production of carbolic acid, the oils which contain it in largest quantity being, as it were, secondary products after the extraction of the hydrocarbons required in the aniline industry.

The preparation of crystallised carbolic acid is a matter of no difficulty, if care is taken in the distillation of the crude acid to collect separately that which passes over between 160° and 190°. This is treated with caustic soda, and the carbolate of soda is then decomposed by sulphuric acid; the oil obtained in this manner only contains very little cresylic acid and naphthalin. By successive rectifications a product is obtained boiling at 180°, and crystallising easily on cooling.

Owing to the large scale on which this body is produced, exceeding, we are assured, 12 tons a week, the price of carbolic acid has been enormously reduced; besides, the value of the product varies with its point of fusion. Carbolic acid fusing at 15° costs 1f. 80c. the kilo.; that fusing at 34° is worth 2f. 20c. the kilo.; whilst that which does not fuse before 41° fetches as much as 10f. the kilo.

* RUNGE, *Ann. de Poggend*, 1834, vol. xxxi., p. 69; xxxii., p. 308.

† A. LAURENT, *Ann. de Chim. et de Phys.*, 3rd series, vol. iii., p. 95.

Amongst the numerous applications of carbolic acid, only that which relates to the manufacture of colouring matters interests us here. We will point out, however, some of its other applications.

In the crude state, it is used for the preservation of wood employed in the construction of railway sleepers and in ship building. In a greater state of purity carbolic acid is employed to prevent and arrest the decomposition of easily putrefactive animal and vegetable substances. It serves in the injection of corpses, the preservation of skins, bones, the different stages of the manufacture of parchment, catgut, glue, gelatine, and lastly, for rendering down fatty matters. It is also advantageously used to preserve paste and starch, and it is of great importance in the disinfection of sewage, tan refuse, the waters in which hemp and flax are steeped, the waste liquids of refineries, starch works, and distilleries. Finally, this acid is applied with equal success to the purification of hospital wards and dissecting rooms, the holds of ships, stables, mews, slaughter-houses, privies, &c.

But the largest quantity—about half the production—is consumed in an almost pure state for the manufacture of picric acid and of peonine or coralline.

II. Picric Acid.

The purity and low price of commercial crystallised carbolic acid at the present day, have had a great influence on the manufacture of picric acid. Hardly six years ago most manufacturers found it advantageous to prepare picric acid by treating the crude oil of coal tar, or the resin of the *xanthorrhæa hastilis*, with nitric acid. Now it is entirely prepared from crystallised carbolic acid.

The advantages gained by the employment of pure crystallised carbolic acid, are not only comprised in the facility with which the operation proceeds, and in the economy of nitric acid, the greater part of which was formerly used up in attacking the impurities, but especially in the facility with which the picric acid is purified. All the foreign substances which are produced when the *xanthorrhæa hastilis* resin, or crude coal tar is treated with nitric acid, are

entirely absent; and the yield of picric acid, when pure carbolic acid is used, is almost the theoretical quantity.

The preparation of this substance is effected by carefully introducing, in small quantities at a time, a stream of nitric acid into pure carbolic acid, or into a previously formed mixture of carbolic and sulphuric acids; or, better still, by attacking crystallised sulphocarbolate of soda by nitric acid.

The picric acid, as met with in commerce, is often mixed with foreign substances, such as sulphate of soda, borax, oxalic acid, &c. To detect this adulteration, it has been suggested to treat the product with benzol, which easily dissolves the picric acid, while most of the foreign bodies remain insoluble.

The best proof of the improvements effected in the manufacture of picric acid is the reduction of its price. In 1862, a kilogramme cost from 25 to 30 frs.; to-day it is only worth 10 frs.

III. Derivatives of Picric Acid.

Picric acid is susceptible of certain metamorphoses which have been attempted to be utilised, to supply the wants of the tinctorial industry.

Isopurpuric Acid.—Under the influence of cyanide of potassium, picric acid changes to a red coloured acid, the ammonia salt of which has the same composition as murexid. It has been named isopurpuric acid. At one time this compound was thought to be identical with murexid, but more recent researches have proved that the two bodies are only isomeric.

The preparation of isopurpurates was mentioned in the Reports of the Universal Exhibition of 1862. We shall therefore confine ourselves to the illustration of certain improvements which have been illustrated in the Exhibition of 1867. According to a communication of Dr. C. A. Martius, Messrs. Roberts, Dale, and Co., of Manchester, had already commenced the preparation of large quantities of this substance some years ago. Many specimens were sent at the time to the principal dyers of Glasgow for trial. But the shades furnished by this body were not then the fashion, and their introduction was limited. New experiments appear

to have been attended with a better result, especially in the dyeing of wool and leather; we may state that the samples of merinos exhibited by M. Casthelaz, dyed with his *soluble ruby* (isopurpurate), presented very fine and rich tints.

The facility with which the isopurpurates detonate with the least shock, renders it necessary to supply these products in the form of paste, containing a certain quantity of water. During the first essays made by Messrs. Roberts, Dale, and Co., a terrible explosion took place in their laboratory during the powdering of 4 or 5 kilos. of isopurpurate of potash, the violence of the explosion was such as to smash all the apparatus in the laboratory, and the workman who was performing the operation was hurled to the ground. Even the paste does not present all the guarantees of security, for drying restores its explosive properties. To remedy this serious inconvenience, Dr. Martius suggests the addition of a small quantity of glycerin, which keeps the substance always wet.

The low price of picric acid allows this product to be sold in paste (with 50 per cent of water), at 11 or 12 frs. the kilo. We feel justified in anticipating soon a considerable demand for this colouring matter; the tendency of dyers, in fact, is more and more to replace extracts of plants and dyewoods by chemical compounds of a perfect purity; as these have a constant composition, they always yield the same colours under the same conditions.

Picramic Acid.—Picramic acid is also a derivative of picric acid; it is produced when the latter is submitted to the reducing action of sulphide of ammonium. Numerous attempts have, for a long time, been made to apply picramic acid to dyeing purposes; but, although this colouring matter possesses a good tinctorial power, and resists the destructive action of light very well, it has not yet taken a place in commerce.

IV. Rosolic Acid.

This name, given formerly by Runge to a red colouring matter existing in oil of coal tar, is used now to designate a tinctorial substance formed by the action of sulphuric or oxalic acids on carbolic acid. It is generally admitted that this substance is the same as that obtained by Runge.

The first publication on the subject of this product was made by MM. Kolbe and Schmitt, in 1861,* who prepared it by heating a mixture of 1 part of oxalic acid, $1\frac{1}{2}$ parts of creosote, and 2 parts of concentrated sulphuric acid. In a note addressed to the jury of Class XLIV., M. J. Persoz drew attention to the fact that the formation of rosolic acid, by the action of sulphuric and oxalic acids on carbolic acid, was observed by him in 1859, and that MM. Guinon, Marnas, and Bonnet, of Lyon, have carried out commercially, since 1860, the process with which he furnished them.

Coralline and Azuline.—Rosolic acid submitted to the action of ammonia under pressure, at a temperature of 150° , is changed into a red colouring matter, called peonine (coralline). This body, heated to 180° in the presence of aniline, gives rise to a blue colouring matter, called azuline. The discovery of these two colours is due to M. Jules Persoz, and patents for their preparation were taken out in 1862 by MM. Guinon, Marnas, and Bonnet.

The details of the manufacture, as given by the patent, having been published in the 1862 Exhibition report, we shall not give them here; but will only add, that experience has shown that to obtain the finest shades and best yield, there must be used carbolic acid, boiling at a constant temperature of 184° , and perfectly dry oxalic acid.

The rosolic acid which is met with in commerce, is in the form of a brittle resin of a cantharides lustre, or in fine powder of a brownish red colour.

Experiments made with the view of applying pure rosolic acid to tinctorial purposes, have not been crowned with success. Of the two colouring products derived from rosolic acid, only peonine (coralline) has acquired a certain commercial importance. Its principal uses are in silk dyeing, calico printing, and the production of lakes employed in the manufacture of tinted papers and lithographic colours.

The blue colouring matter formed by the action of aniline on peonine is no longer made, being replaced in commerce by aniline blue.

* KOLBE and SCHMITT, *Ann. der Chem. u. Pharm.*, lxi. 169.

DERIVATIVES OF NAPHTHALIN.

I. Naphthylamine Yellow.

Amongst the numerous processes which have been pointed out for the transformation of naphthalin into colouring substances, only one has been commercially applied. This process, which we owe to Dr. C. A. Martius, enables us to obtain a magnificent yellow colouring matter, which, in France goes under the name of *jaune d'or*, and in England, of Manchester yellow.

Naphthalin is obtained in the distillation of coal; it is principally found in the heavy oils which remain after the separation of the hydrocarbons which yield benzol, toluol, and the phenols.

The quantity of naphthalin produced in the distillation of coal appears to vary according to its nature, and the plan of carbonisation followed. It forms a residue in gasworks, especially in those where tar is manufactured either for the preparation of hydrocarbons, or for the manufacture of artificial fuel.

When treated by similar processes to those already described for the transformation of benzol into nitro-benzol and aniline, naphthalin furnishes nitronaphthalin and naphthylamine, a base analogous to aniline, and which forms the starting point for the production of Manchester yellow. To prepare this, a neutral solution of hydrochlorate of naphthylamine is added to nitrite of soda, until all the naphthylamine is transformed into diazonaphthol. The liquid which contains the hydrochlorate of diazonaphthol is mixed with nitric acid, and heated to ebullition. The yellow colouring matter separates and floats on the surface in the form of small yellow needles, which are collected with a large skimmer. To purify it, it is dissolved in ammonia and filtered.

According to the experiments of Dr. Martius, this yellow compound is binitronaphthol, which stands in the same relation to naphthalin as binitrophenol does to benzol. It is an acid analogous to picric acid, and forms with bases

salts which are, for the most part, well crystallised, and possess a more or less orange colour. Binitronaphthylic acid is already employed extensively in dyeing wool and leather; it is also used to colour many other substances, amongst which we may name soap.

This colouring body is remarkable for the brilliant golden yellow shades which it communicates to fabrics, and which are easily distinguishable from those given by picric acid, the latter yielding much greener tints. This is not the whole advantage which it possesses over picric acid; the tints which it furnishes admit of being steamed, whilst, on the contrary, those given by picric acid are destroyed by this operation.

Hitherto the very high price of binitronaphthylic acid (50 francs the kilo.) has prevented its general adoption as a dye. We should, however, remark that for equal weights its tinctorial power is much greater than that of picric acid.

II. Benzoic and Chloroxynaphthalic Acids.

Attempts have recently been made to utilise naphthalin as a source of benzoic acid, a substance which, as already stated (page 124), is often employed in the transformation of rosaniline into the blue colouring matter. These experiments are the more interesting, as they have given rise to the production of secondary products capable of being applied to dyeing and calico printing. Hitherto benzoic acid has been extracted either from gum benzoin, or from the hippuric acid contained in the urine of herbivorous animals. It has now been proposed to prepare it by decomposing phthalic acid, a derivative of naphthalin made known by the researches of Laurent and M. de Marignac.

The composition of phthalic and benzoic acids presents a very simple relation. Benzoic acid contains the elements of phthalic acid, minus one molecule of carbonic acid. Between these two acids there is the same difference of composition as between benzoic acid and benzol, a hydrocarbon which can be produced by removing one molecule of carbonic acid from benzoic acid.

It was known that when phthalic acid is submitted to the action of lime with the agency of heat it splits up into benzol and two molecules of carbonic acid. It was therefore probable (and Gerhardt, and more recently Berthelot, had pointed this out) that phthalic acid could be transformed into benzoic acid by arresting the action, as it were, half way. M. Dusart* tried to effect this decomposition; but although, on distilling a mixture of phthalate and oxalate of soda with lime, he succeeded in obtaining a small quantity of oil of bitter almonds, he did not succeed in transforming phthalic acid into benzoic acid.

This reaction has been since effected by MM. P. and E. Depouilly.† They took one molecule of bicalcic phthalate, and one molecule of hydrate of lime, and heated the mixture for several hours to a temperature of from 330° to 350° ; the salt is then entirely converted into benzoate and carbonate of lime. The benzoate of lime is dissolved in water, the solution concentrated, and the benzoic acid precipitated by an acid. Laurent described phthalic acid in his great work on the derivatives of naphthalin, published in 1832 to 1845. He obtained it by oxidising the chlorine substitution products of naphthalin with nitric acid. The following is the plan which MM. P. and E. Depouilly finally adopted:—Naphthalin is treated in the cold with a mixture of chlorate of potash and hydrochloric acid. In this manner by one operation are obtained a large quantity of quadrichlorides of naphthalin and chloronaphthalin, together with a very small quantity of subchlorides; these latter are removed by pressure. The solid residue, which is a mixture of quadrichloride of naphthalin and of quadrichloride of chloronaphthalin, is attacked by nitric acid on a water bath. The former changes into phthalic acid, and the latter into chloride of chloroxynaphthyl, which, by modifying the temperature, also gives phthalic acid. The mixture of chlorate of chloroxynaphthyl and of phthalic acid is extracted with boiling water, which only removes the phthalic acid.

* Comptes Rendus de l'Académie, 1862, lv., 44.

† Comptes Rendus de l'Académie, lx., 456.

The chlorate of chloroxynaphthyl is capable of yielding a beautiful crystalline substance of a very brilliant orange yellow colour; this is the chloroxynaphthalic acid of Laurent. To obtain this acid the chloride of chloroxynaphthyl is treated with an alcoholic solution of potash, which transforms it and dissolves it in the state of chloroxynaphthalate of potash.

The solution is decanted or filtered from the residue, and decomposed by a mineral acid. Chloroxynaphthalic acid deposits, but in an impure state; to purify it it is transformed into a neutral potash salt. This is treated with a solution of alum, which precipitates a brown colouring matter differing from chloroxynaphthalic acid in colour. The filtered liquid precipitated by a mineral acid deposits chloroxynaphthalic acid in the form of a crystalline powder of a pale yellow colour, which colours wool an intense red without a mordant. This substance is very beautiful, and will probably meet with important applications in dyeing and printing. Unfortunately, the process by which it is obtained is very long and costly, and consequently the price of the product is high.

In conclusion, we may perhaps be permitted to direct anew the attention of manufacturers to chloroxynaphthalic acid, which is perhaps destined to play an important part in the history of artificial colouring matters. In his *Traite de Chimie Organique*, Gerhardt* pointed out the very simple relation which existed between the composition of chloroxynaphthalic acid and of alizarin, the colouring principle of madder. Indeed, by replacing the chlorine in chloroxynaphthalic acid with an equivalent of hydrogen, we obtain the formula of alizarin.† All experiments which have hitherto been tried to effect this important transformation have failed. Doubts have even been expressed as to the possibility of ever succeeding in it; at the same time all hopes of seeing this change realised ought not to be abandoned.

* GERHARDT, *Traité de Chimie Organique*, iii., 478.

† Chloroxynaphthalic acid $C_{10}H_5ClO_3$
 Alizarin $C_{10}H_6O_3$

OTHER APPLICATIONS OF THE COAL TAR COLOURING MATTERS.

The other applications of these colours are numerous, and although they do not consume so large quantities as are used in dyeing, they still deserve some attention. It is always interesting to follow the attempts made by manufacturers to adapt to the most varied wants every new substance which enters their domain, to multiply its applications, and thus to force it to yield up the sum total of utility which it virtually contains.

Since 1862, the paper-maker has used large quantities of aniline colours either to blue his pulp, to tint it, or to communicate a superficial colour to paper when finished. Their solubility in water has caused their use rapidly to extend, and now they have almost entirely replaced all the substances which were formerly employed, such as ultramarine, different metallic oxides, extracts of wood, &c. Of all the aniline colours, that most used in paper-making is the soluble blue. It may be used either by mixing its aqueous solution direct with the paper pulp, or when it is sized.

Many objects of stationery are ornamented by means of these colours, such as the designs in imitation of porcelain. These are made by printing a design on a sheet of ordinary paper by means of a lake of aniline dye dissolved in a salt of aniline. This is then taken off on to a sheet of paper strongly albuminised and damped. The colour is fixed with albumen, and a pretty looking reproduction of the original design is thus obtained with rich full tints.

Most wafers, powders for drying ink (sand, pounce, &c.,) are coloured with aniline dyes. Certain coloured inks, especially the red and violet inks, are manufactured from salts of rosaniline and methyl-rosaniline. They are generally aqueous solutions containing a sufficient quantity of gum or dextrine, and containing a little glycerin. They are very rarely formed of lakes held in suspension.

Inks for typography are also made with these substances. One of the first processes employed consists in dissolving

the colours in alcohol containing a resin in solution, and then precipitating the whole by water. The dried precipitate is ground up with a suitable quantity of varnish and zinc or baryta white. Another process consists in mixing with varnish, starch coloured with the aniline dye. A third is to precipitate the colouring matter with an alkali so as to obtain the base; the dried precipitate is dissolved in oleic acid, and then mixed with a lithographic varnish free from lead.

The aniline dyes are also utilised in the manufacture of lakes to be used in staining or colouring paper, in water colour painting, in colouring designs and especially photographs. For this latter purpose they have the advantage of being perfectly transparent, of allowing the most minute details to be seen, and of forming an intimate combination with the albuminised paper used in photography. They are prepared by taking advantage of the property they possess of combining with certain metallic oxides or other substances, such as kaolin, starch, tannin, &c. With this object, a soluble salt of the colouring substance is precipitated by a solution of a metallic salt, the oxide of which forms an insoluble compound with the acid of the colour salt; or better still, by precipitating mixed solutions of the colouring matter and metallic salt by ammonia or carbonate of soda. The best lakes are obtained when the precipitation of salts of aniline red, violet, or blue is effected in the presence of benzoic acid. Starch, kaolin, and alumina, added to solutions of these dyes, decolourise them rapidly, absorbing all the colour, and becoming tinted in the same manner as silk or woollen fabrics. Tannin precipitates aniline red very completely from its aqueous solutions, and forms with it an insoluble lake of a fine carmine colour; sulphate of alumina is sometimes mixed with the tannin. The following is the plan ordinarily adopted:—Carbonate of soda is mixed with sulphate of alumina so as to exactly neutralise the liquid without precipitating it; the solution of the colouring matter is then added, and the whole is precipitated with tannin. The coloured powders so largely employed in the manufacture of flock paper for wall decoration, are prepared by grinding up woollen

shreds, and dyeing them in various tints of aniline colours by the ordinary processes. Most of these lakes, mixed with drying oils or varnish, may also be used in the preparation of printing inks.

A method of laquering wood, in which the metallic reflection possessed by these colours in the solid state is preserved, is effected by immersing the wood in hot concentrated alcoholic solutions of the aniline dyes. The wood is rapidly dried in a current of warm air, and then coated with a transparent varnish made of copal dissolved in ether. Owing to its insolubility in this vehicle, the colouring matter preserves all its lustre, and is protected from moisture and friction by the hard, insoluble, adherent pellicle which the varnish leaves on drying. These processes have lately been applied to the dyeing and coloration of straw for bonnets, and to the manufacture of artificial leaves. The process is similar to that described for laquering wood.

The aniline dyes are equally applicable to the decoration of glass and porcelain, when required exclusively for ornamental purposes. They are applied by dissolving in alcohol, and painting on with a brush, and are afterwards coated with a transparent resinous varnish insoluble in water. Objects so decorated look like enamels, but have neither their quality nor permanency. In this list of secondary applications, one must be mentioned which employs considerable quantities of these colours; this is the decoration of glass globes used for public illuminations. They are prepared by dipping the globes in a solution of albumen, blood, or gelatin, and then removing and drying them; they are then passed through a bath of the dye. In this way globes are obtained possessing the same lustre as glasses coloured with cobalt or purple of Cassius.

Pearls and precious stones are imitated by a similar process more carefully carried out. The same plan is adopted for the coloration of mother of pearl, ivory, bone, and other substances of animal origin. These, however, are able, partially, to combine direct with the colouring matter.

The art of perfumery also has recourse to the aniline dyes for the coloration of essences, soaps, cold cream,

pomades, rice-powder, &c. Their application to these different uses is self-evident; and, granting the utility (a very questionable one) of the unguents with which the fair sex love to anoint themselves, we are constrained to admit that the introduction of the aniline dyes to this branch of industry has been of undoubted service. They have superseded the metallic substances—the preparations of mercury, of bismuth, and of lead—which were almost all injurious to health. As, however, it is not our wish to destroy pleasant illusions, we shall not enter into more ample details on so mysterious a subject.

To abridge this enumeration, already too long, of the trades employing the aniline dyes, we will content ourselves with mentioning the blueing of linen, the tinting of candles and wax vestas, the coloration of white vinegar to imitate wine vinegar, and lastly the fabrication of syrup of raspberries in America.

A few words are required for a recent scientific application. Aniline red, blue, and violet, dissolved in water or dilute alcohol, are daily employed by microscopists for the soaking of tissues, of which the anatomical elements are coloured unequally, so that some of them become more visible under the microscope. Carmine dissolved in ammonia was formerly employed for this purpose, but the aniline colours are preferable in many cases where the delicacy of the tissues would be unable to resist the action of ammonia.

In a similar manner M. C. Legros uses the red, blue, and violet to colour collodion with which he injects the vessels of men and animals for anatomical purposes. This injection is very penetrating, and permeates the most delicate capillaries, whilst at the same time the colours preserve all their brilliancy without injuring the transparency of the tissues. Specimens injected in this manner may be preserved very well in glycerin. This injection may be employed cold, and admits of the anatomical specimens being dried quickly.

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I N D E X .

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